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THE CHEMICAL SAMPLING AND ANALYSIS OF C.W. AGENTS USED IN FIELD EXPERIMENTS

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PORTON MEMORANDUM No. 19A

C.D.E.E.
Porton.
Wilts.

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PORTON MEMORANDUM NO. 19A

COPY NO: 37

DATE: 23 MAR 1956

THE CHEMICAL SAMPLING AND ANALYSIS OF C.W. AGENTS

USED IN FIELD EXPERIMENTS

INTRODUCTION

Porton Memorandum No. 19 published in 1942 described the methods of sampling and analysis of C.W. agents which were in use at that time.

With the normal developments of time and particularly due to the advent of the G gases, the emphasis in field experiments has changed considerably and P.M. 19 is now seriously out of date. The number of samples taken per trial has been increased enormously, and sampling in miniature bubblers at 1 litre per minute has been introduced. Many sampling devices and methods of analysis have become obsolete, and some of these have been replaced and others abandoned because the compounds for which they were devised are no longer of prime interest.

This memorandum has therefore been compiled to replace P.M. 19. It includes all the methods which are now in regular use and also some which are used infrequently. Others are included because of their suitability for use in isolated cases, although these have not been brought up to date (Jan. 1955), and as a guide to the modernity of the method, the date of the last use is given in the heading.

The memorandum was compiled by D. Thorp.

DT/JMP.

(Sgd.) E. A. Perren,
Chief Superintendent.

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SECTION I

TABULAR SUMMARY

This is a brief summary in tabular form of the present (January 1955) position of the methods of collecting the various samples, the analytical methods employed and the sensitivity obtainable.

The sensitivity (as Ct.) depends on both the analytical method and the sampling technique, since the efficiency with which the sample is utilised in the analytical method plays a vital part. Thus, if the volume of the aliquot of sample used in the analysis is already at the maximum suitable for use in the largest size of absorptionmeter cell, and the only way of increasing the size of the sample entails a corresponding increase in the volume of sampling solvent, there is no real advantage to be gained by increasing the size of the sample. Conversely, in some cases, a change from a 10 litre/min. sampling rate to a sampling rate of 1 l/min. will reduce the sensitivity (i.e. increase the lower limit measurable by the method) by 10 times, but in other cases where, when the flow rate is reduced, the volume of sampling solvent can also be reduced, this reduction in sensitivity will not be so great.

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SECTION I

SUMMARY OF SAMPLING TECHNIQUES, ANALYTICAL METHODS AND LOWER LIMITS OBTAINABLE IN THE ANALYSIS

Substance	Collection of the sample	Maximum aliquot	Analytical Method	Lower limit of analysis μg in sample	Ct.	Date of last use of method
ACETYLENE	Bead bubbler 20 ml. Acetone 2 l/min.	1/2	Copper SPEKKER	10	5	1953
AMMONIA	Miniature Bubbler 5 ml. 0.01 N.HCl 1 l/min.	ALL	Nessler SPEKKER	5	5 (up to 200)	1954
ANILINE	Miniature Bubbler 2 ml. 50% Acetic Acid 1 l/min.	ALL	p dimethylamino- -benzaldehyde SPEKKER	2	2	1954
ARSENIC	Bead Bubbler 15 ml. 5% NaOH 10 l/min.	ALL	Evolution of arsine, then absorb and oxidize. Molybdate, stannous chloride method. SPEKKER	10 as 'Is.	1 as As.	pre 1946
Methyl dichloro- -arsine Ethyl dichloro- -arsine	Filters 10 l/min.					
DA, DC, DM, etc.	Filter backed by bubbler 10 l/min.					
Lewisite	Filter backed by bubbler 10 l/min.					
ARSINE	Bead bubbler 15 ml. 3% Silver nitrate 10 l/min.	ALL	Silver is precipitated, dis- solved in nitric acid and titrated with KONS	25	2.5	pre 1946
BROMOCHLOR- CYANIDE	Bead bubbler 15 ml. Alcohol 10 l/min.	ALL	4,6. dichloro 1,3. dinitro- -benzene SPEKKER	5	0.5	pre 1946

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Substance	Collection of the sample	Maximum aliquot	Analytical method	Lower limit of analysis µg in sample	Date of last use of method
CARBON MONOXIDE	Balloon Evacuated Bottle Aspirator etc.	ALL	Infra Red Gas Analyser	-	1955
			Reduction of iodine pentoxide and titration	300	1953
CHLORINE	See Chlorine, Phosgene etc.				
CHLORINE	Large sintered bubbler 60 - 180 ml. sodium arsenite 25 - 40 l/min.	ALL	Potentiometric titration of chloride	-	1951
	Miniature bubbler 4 ml. sodium arsenite 1 l/min.	ALL	- do -	30	1951
	Bead bubbler 15 ml. 0.002 N NaOH 2 l/min. Slip bubbler required	ALL	o - toluidine SPEKKER	2	1951
CHLOROACETO - - PHENONE	Bead bubbler 20 ml. 80/20 alcohol/ glycerol 10 l/min.	1/5	m-dinitrobenzene SPEKKER	50	1953
	Bead bubbler 15 ml. alcohol 10 l/min. Slip bubbler required	1/2	β naphthol and crotonaldehyde SPEKKER	50	pre 1946
CHLOROSULFONIC - ACID	On sand in a bottle (for large drops - fallout near source)	ALL	Titration with 0.1 N NaOH and with 0.1 N. mercuric acetate	4,000	pre 1946
	Filter backed by a bubbler charged water 10 l/min.	ALL	Titration for total acidity with 0.1 N NaOH Potentiometric titration for chloride	1,000	pre 1946
CYANIDE	See Hydrogen cyanide, CA etc.				

Substance	Collection of the sample	Maximum Aliquot	Analytical Method	Lower limit of analysis µg in sample	Analysis Ct.	Date of last use of method	
CYANOGEN CHLORIDE	Large sintered bubbler 100 mL, 4% alcoholic NaOH 40 l/min.	ALL	Titration with 0.1 N silver nitrate	1,200	30	1951	
	Miniature bubbler 2.5 mL, benzidine in pyridine 1 l/min.	ALL	Benzidine - Pyridine SPEKKER or UNICAM	1	1	1951	
DICHLORODIETHYL - ETHER	Bead bubbler 15 mL, pyridine 10 l/min.	1/2	Pyridine SPEKKER	25	2.5	1946	
DYE (characteriser)	Envelope, Felt pad, Turf, Soil from crater Sand Cascade impactor slide		SPEKKER or UNICAM	5,000 µg charging on 4% Wax, Red 2,000 µg charging on 2% Violet 3809		1954	
ETHYLCHLOROACETATE	Dimple bubbler 20 mL, 5% NaOH 10% alcohol 10 l/min.	ALL	Hydrolysis and potentiometric titration of chloride	100	10	1948	
FERRIC CHLORIDE	Filter 1 l/min. or 10 l/min.	3/4	Thioglycollic acid	7 or 7	7 or 0.7	1952	
FLUORIDE	e.g. GB in dimple bubbler charged 20 mL, N. NaOH 10 l/min.	1/10	Amperometric titration	100 as F ⁻		1953	
		ALL	Titration with thorium nitrate using solochrome blue	5 as F ⁻ 40 as GB	4	1946	
FURFURAL	Miniature bubbler 5 mL, 10% aniline in 50% acetic acid 1 l/min.	ALL	Visual observation only. The method could probably be made quantitative by sampling in 50% acetic acid and then adding the aniline later. As used for demonstrations the colour fades after an hour or so.				1954
G Series	GA only	1/4	As cyanide Benzidine pyridine	10 as GA	1	1948	
	Dimple bubbler 10 l/min. 20 mL, N.NaOH miniature bubbler 1 l/min. 2 mL, N.NaOH				2.5 as GA		2.5

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Substance	Collection of the sample	Maximum aliquot	Analytical Method	Lower limit of analysis µg in sample	Limit of analysis Ct.	Date of last use of method
G Series (Continued)	Dimple bubbler 10 l/min. 20 ml. N ₂ NaOH	1/4	As phosphate Molybdate, stannous chloride	8 as P	0.8 as P	1951
	Miniature bubbler 1 l/min. 2 ml. N ₂ NaOH	ALL	SPEKKER	2 as P 10 as GB	2 as P 10 as GB	
	Miniature bubbler 2 ml. cyclohexanol 1 l/min.	ALL	Dianisidine, peroxide	5	5 (up to 1300)	1955
	Miniature bubbler (all glass) 2 ml. cyclohexanol 1 l/min.	ALL	SPEKKER	0.4	0.4 (up to 50)	
HYDROGEN CYANIDE	Dimple bubbler 20 ml. N ₂ NaOH 10 l/min.	ALL	Titration with silver nitrate	1,000	100	1954
	Filter 10 l/min.	1/4	Benzidine, pyridine SPEKKER	2	0.2	1954
INSPECTICIDAL SMOKES (a) DDT and HCH	Filter 10 l/min.	ALL	Hydrolysis and potentiometric titration of chloride	500	50	1952
(b) INOC	Filter 10 l/min.	ALL	Colour with caustic soda SPEKKER	20	2	pre 1946
MANGANESE SULPHATE	Miniature bubbler (all glass) 5 ml. specially distilled water 1 l/min.	ALL	Oxidation with periodate Colour with tetrabase SPEKKER	0.02	0.02 (up to 2)	1953
METHYLACETOACETATE	Miniature bubbler 5 ml. water 1 l/min.	ALL	Triazotise and couple with 2,5 dichloroaniline SPEKKER	2	2 (up to 10,000)	1954
METHYL SALICYLATE	Bead bubbler 15 ml. 0.1 N NaOH 10 l/min.	2/3	Phosphotungstomolybdate SPEKKER	30	3	1948

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Substance	Collection of the sample	Maximum aliquot	Analytical Method	Lower limit of analysis ug in sample	Number of analysis Ct.	Date of last use of method
MUSTARD GAS	Miniature bubbler (all glass) 5 ml cyclohexanol 1 l/min.	ALL	DB-3, heat to 80°C SPEKKER	5	5 (up to 16,000)	1954
	Miniature bubbler two in series 5 ml, 50% acetic acid 1 l/min.	ALL	Titration with Bromine solution using methyl red or electrochromic end point	50	50	1954
NICKEL (characteriser)	Silica gel tube 10 l/min.	ALL	Potentiometric titration of chloride	150	15	pre 1946
	Felt pad. Turf, sand or earth from crater		Wet oxidation and then dimethyl glyoxime	Varies	-	1950
NITROGEN MUSTARDS	Bubbler DB-3 reagent		DB-3	Not tested	-	
NITROUS FUMES	Evacuated bottle containing 15 ml, 5% NaOH	2/5	α naphthylamine and sulphanilic acid SPEKKER	2 as gas	-	1954
ETHYL - α NAPHTHYLAMINE (characteriser)	Envelope Cascade slide etc.	ALL	Diazotised sulphanilic acid, and couple. SPEKKER	0.2	-	pre 1946
PHOSGENE	Dimple bubbler 20 ml 2% NaOH 1% hexamine 10 l/min.	ALL	Potentiometric titration of chloride	50	5	1952
	Miniature bubbler 2 ml, 1% hexamine 2% NaOH 1 l/min.	ALL	- do -	50	50	
PHOSPHORUS SMOKE	Filter 10 l/min.	4/5	Molybdate method SPEKKER	1 as P	0.1 as P	1951

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Substance	Collection of the sample	Maximum aliquot	Analytical Method	Lower limit of analysis µg in sample	Number of analyses Ct.	Date of last use of method
SALICYLALDEHYDE	Blue asbestos filter 10 l/min.	ALL	Colour with caustic soda SPEKKER	20	2	1953
SULPHUR DIOXIDE	Miniature bubbler 5 ml. water 1 l/min.	ALL	Basic fuchsin and formaldehyde SPEKKER	2	2 (Up to 200)	1953
ZINC (smoke)	Petri dish etc.	ALL	Amperometric titration with quinaldinic acid	8		1954

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SECTION II
COLLECTION OF THE SAMPLE

A. ABSORBING OR TRAPPING APPARATUS

1. APPARATUS FOR SAMPLING GASES

(a) BUBBLERS

(1) The Miniature Bubbler (1 Litre/min.)

The miniature bubbler consists of a glass tube about 6" long and 0.5" diameter, closed at the bottom and with a bulb in the centre so that the volume to a point just above the bulb is 25 ml. and the tube below the bulb is about 2.5" long. The bubbler is graduated at the 25 ml mark, and has a short side arm near the top to which the suction is applied. The inlet to the bubbler consists of a glass capillary tube of 1.0 to 1.5 mm bore and 5.0 to 6.5 mm diameter which is inserted into the top of the bubbler by means of a rubber bung, and terminates $\frac{1}{4}$ " from the bottom of the bubbler.

Each bubbler is numbered individually and permanently. The inlet tube bears the same number and when assembled normally the bubbler is connected by means of a U bend to a critical orifice which also carries this number (Fig.1).

The bubbler is usually charged with 2 ml of solvent and it has been shown that when sampling at 1 litre/min. no droplets larger than 3 μ will pass through the bubbler. The efficiency of absorption in the bubbler is dependent on the volume of sampling solvent, the time of sampling, and on the temperature, as well as on the gas sampled and the solvent used.

The complete assembly of bubbler and critical orifice is checked for flow rate in the laboratory before each trial (Fig.2).

The bubblers are mounted on metal frames, which have replaced the wooden boards used originally, either singly, in pairs, or in groups of 3 or 4 and carried in slotted boxes (Figs. 3 and 4).

This assembly is very convenient for field use, installation and protection, a single bubbler being both supported and protected by a piece of angle iron, whilst the suction leads are buried and the pumps and batteries protected by being placed in shallow pits, or by sandbags (Figs. 5 and 6).

Current drawings are as follows:-

Bubbler	OD.5712
U bend	SK.1685
Metal holder	
single	OD.5755
double	OD.5756
triple	OD.5757

Bubbler protectors

When sampling in rain, or when it is desired to exclude liquid droplets of the agent (e.g. when taking sequential samples and the bubblers in which the later samples are to be collected are emplaced before the weapon is functioned) protectors are required.

Much thought has been given to this problem and several devices have been tested. These have included empty cartridge cases with slots cut in the sides to admit the air, conical metal caps supported by a wire which was bent round the bubbler stem, glass U bends, etc., none of which was completely satisfactory.

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With the glass U bends, the air entered vertically upwards, but it was found that when sampling was carried out in heavy rain the drop which collected at the end of the inlet was sucked into the sample. It was then suggested that the glass should be treated with silicone to alter the surface tension, but in the meantime polythene U bends had been tried and these have proved satisfactory, provided that the diameter is fairly wide ($\frac{3}{8}$ inch internal) and the bubblers are kept reasonably vertical so that the drops can fall off the end of the polythene, before being sucked into the sample.

The All-Glass Miniature Bubbler

A certain amount of trouble has been experienced with the miniature bubblers, particularly when they are used to sample low concentrations of G gases, or for mustard gas. This was found to be due to traces of rubber from the rubber bungs getting into the sample either mechanically or by solvent action, leading to erratic results.

All-glass bubblers, in which the capillary inlet tube is fitted into the bubbler by a ground glass joint, have now been introduced for these purposes and are expected to replace the bung bubblers generally.

Drawing CD. 6132

(2) The Dimple Disc Bubbler

This bubbler has now been superseded by the miniature bubbler for many purposes, but it may still prove useful when an increase in the volume of sampling liquid is required, and when the number of samples is not so great that its use is precluded on the grounds of size (transport, etc.).

The dimple disc bubbler largely replaced the bead bubbler (see below) owing to its much greater robustness and ease of washing out.

The bubbler consists of a glass cylinder 8" to 9" high and $\frac{1}{4}$ " diameter with the whole of the walls up to 5" high dimpled to give internal spines and therefore an increased absorbing surface. The inlet tube is sealed into the top of the bubbler and runs inside the body to the bottom where it splays out into a disc about $\frac{1}{2}$ " diameter and $\frac{1}{8}$ " from the bottom of the bubbler. About $\frac{1}{4}$ " from the bottom of this inlet tube there is a similar disc to break up the bubbles further. (Fig. 7)

The bubbler is charged with 20 ml of solvent and is normally used for sampling at 10 litres/min. Two bubblers are carried in an aluminium crate and 13 crates in a wooden box. (Fig. 8)

Drawing Ptn/1600 (U8697)

(3) The Bead Bubbler

This bubbler, although fragile and difficult to wash out gives more efficient absorption than the dimple bubbler (or the miniature bubbler), i.e. it has a much lower "slip". It has therefore been retained for certain gases, e.g. acetylene, which are difficult to absorb.

The bead bubbler is a glass cylinder 10" high $\frac{1}{8}$ " diameter, divided into halves by a constriction down to $\frac{1}{4}$ " width (internal) and with the lower half filled with $\frac{5}{16}$ " diam glass beads. The inlet tube $\frac{1}{4}$ " i.d. connects to the bottom of the bubbler and is brought up by suitable bends to a position just below the level of the neck (Fig. 9).

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This bubbler is charged with 10 to 20 ml of sampling solvent and can be used at flow rates up to 10 litres/min.

Drawing CD.5711

(4) The Large Sintered Disc Bubbler

This consists of a glass cylinder 3" in diameter and 10" high with an inlet tube $\frac{3}{4}$ " diameter down the centre of the bubbler terminating in a fritted disc about $\frac{1}{4}$ " from the bottom of the bubbler and with a narrow annular space around it. A wide outlet tube and a stoppered filling hole are provided.

The minimum volume of sampling solvent, since the frit must be completely covered, is 60 ml and the bubbler is normally operated at sampling rates of 30 litres/min. and over.

It has proved useful in cases where the sampling rate could not be reduced below 30 litres/min., e.g. in simulated breathing experiments. It has a very small slip.

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(b) TUBES FOR SOLID ABSORBENTS

The tube usually used is of plastic and tapered slightly, approximately 2" by 1" outside dimensions, with a copper gauze closing one end and with a screwed collar of the same plastic material at the other end. The tube is filled with 5 cc of silica gel or 3 cc of charcoal, which rests on the bottom gauze and is held in position by a second gauze and a light spring which is retained by the screwed collar. It is possible to incorporate a dust filter under the collar, but such filter must have a low flow-resistance, and a small absorptive capacity for the agent under consideration (Fig. 10).

A plastic tube of a different shape, to hold roughly the same amount of gel, but with a shorter path length for the air being sampled, has a lower air resistance and has been considered for use in some cases, e.g. when operated by human breathing.

The advantages of the tube sampler over the bubbler are portability (non-spill), strength and lightness.

Solid absorbents have been used to sample mustard gas (to be estimated by the non-specific chloride method). Silica gel was used in temperate climates, but an activated charcoal filling was used in the tropics, since in the warm humid atmosphere the silica gel became saturated with water and the slip of the mustard gas through the tube became excessive.

Silica gel has been used to sample GB and GE for analysis by the dianisidine method, but only where the samples could be analysed immediately to avoid loss of G by hydrolysis.

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(c) SAMPLERS NOT RELYING ON ABSORPTION

The main use of this type of sampling apparatus is for gases which are difficult to absorb, and therefore cannot be sampled conveniently in bubblers. They have been used recently for nitrous fumes and for carbon monoxide.

(1) The Evacuated Bottle

A Winchester glass bottle ($2\frac{1}{2}$ to 3 litre) with an accurately measured internal volume is fitted with a bung and a length of pressure tubing. After evacuation the tubing is closed by a screw clip, and a glass plug, or a glass jet drawn out to a sealed point, is inserted in the tubing as an additional seal. The screw clip is released before sampling and either the plug removed or the glass jet broken at the correct moment. The bottle takes about 4 seconds to fill and is resealed as soon as possible after sampling (Fig. 11).

Evacuated bottles have been used to sample from positions inaccessible to the bottle by means of a length of tubing leading to the sampling point. Immediately prior to sampling a hand pump is operated for a number of strokes calculated to clear this tube, and the tube is then connected to the bottle before releasing the screw clip.

For some gases it is necessary to add a reagent to absorb the gas. With aqueous solutions this can be done before evacuation provided that the pump is fitted with a suitable drying trap. The absorbing solution is then swirled round to wet the sides of the bottle before and after the sample has been taken.

(2) The Balloon Inside a Bottle

The Winchester bottle is closed by a bung through which pass two short metal tubes. From one of these tubes a piece of rubber tubing leads to the bottom of the Winchester and the other end is attached through a critical orifice to a pump. To one end of the other metal tube is attached a balloon which hangs limply inside the bottle, whilst the other end of this tube is connected to the sampling position.

When the pump is switched on, the air is drawn out of the bottle, causing the balloon to inflate and draw air from the sampling position. At the end of the sampling period both tubes leading from the bottle are closed by means of a piece of glass rod.

Both 25 gram meteorological balloons and strong toy balloons have been used to sample for 5 minutes at 0.5 litres/minute. One T1 pump can be used to operate 10 or 20 sampling positions.

In a few cases with long shaped balloons it was advisable to omit the rubber tubing inside the Winchester.

(3) The Water Filled Bottle with a Syphon Tube

The Winchester bottle is filled with water and closed by a bung through which pass two tubes reaching almost to the bottom of the bottle. One of these is slightly longer than the other and is bent over outside the bottle to form a syphon tube, the other is the sample inlet and is connected to the sampling position. With this constant head device, the sampling rate is roughly constant and samples can be taken for moderate periods e.g. 5 minutes at 0.5 litres/min.

(4) The Aspirator

Two aspirators (usually 10 litre) are used connected together by rubber tubing with a screw clip. Water is allowed to flow from one to the other at a steady rate and so collects the sample in the aspirator from which the water is flowing. Care must be taken to equalise the pressure in both aspirators, before and after sampling, in order to measure the volume collected.

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The main purpose of this device is to take a continuous sample at a regular speed of a not readily absorbed gas, such as carbon monoxide.

(5) The Football Bladder

The bladder is fitted with a non-return valve (the usual type of valve adaptor for inflating footballs by a bicycle pump) and attached to the outlet of the pump. The critical orifice is attached to the inlet of the pump and forms the sample intake.

Only diaphragm pumps are suitable for use with this technique and even these should be tested for leaks to ensure that the amount of air blown into the football is the same as that collected from the sampling point. A slight leak is immaterial provided that the sampling position is large enough to accommodate the whole pump and not just the inlet, so that the air leaking in is identical with the sample.

A convenient sample for a football bladder is 10 litres and T1 pumps have been used to take samples for 30 seconds, at 20 litres/minute.

Only one sample can be taken by each pump and the sample is slightly contaminated by lubricant etc., during passage through the pump. If an appreciable time is expected to elapse between sampling and analysis, the neck of the bladder should be plugged as the non-return valves are not very efficient.

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2. APPARATUS FOR SAMPLING PARTICULATE CLOUDS

THE DOUBLE CONE FILTER

This consists of two plastic cones which are threaded at the wide end so that one can be screwed into the other. A standard sized filter paper, 5.5 cm in diameter, together with a rubber washer, is placed on a ledge inside the outlet cone and held in position by the other cone when this is screwed in. The end of the outlet cone is provided with a ridged tube to give a good fit into the suction tube of the injection (Fig. 12).

If strict isokinetic sampling is considered desirable, a glass tube of the correct diameter can be inserted into the inlet end of the filter (Fig. 13).

The filters are carried in wooden "nests", each of which holds four filters with the ridged ends down, so that the sample is on the top surface of the filter and is therefore less likely to be shaken off in transit back to the laboratory.

When sampling at 10 or 15 litres/min., one Whatman No.1 paper has been found to be satisfactory for white phosphorus smoke, while for the insecticides DDT, benzene hexachloride, and INOC, two thicknesses of Whatman No.1 paper were used. For other smokes, Whatman No.44 paper has generally been satisfactory, but for salicylaldazine an asbestos paper had to be used.

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3. EQUIPMENT FOR THE SAMPLING OF GROUND CONTAMINATION

Four methods of estimation of ground contamination are commonly used:-

- (a) sampling envelopes
- (b) felt pads
- (c) turves
- (d) pie plates or petri dishes

Of these (a) (b) and (c) are normally used simultaneously, whilst (d) may be used to replace any of them according to the circumstances.

The areas of the sampling devices, viz.

Envelopes 17.4 per square metre

Felt pads 100 "

Turves 218 "

are related to the degree of contamination which they are expected to sample. The envelopes, having the largest area, are used for the positions of the lightest contamination when the drops will be more scattered, so that a larger sampling area is required to obtain a representative sample.

(a) THE SAMPLING ENVELOPES

The sampling envelope has one side made of Whatman No.1 filter paper about 9" x 9½", whilst the other side and also a frame round the filter paper is made of moisture resistant paper such as Buff Manilla. Inside the envelope is placed a flat iron plate with a rim 3/16" high, to provide weight to prevent the envelope from being blown away and also to act as a spacing ring to give an air gap below the filter paper so that the liquid droplets will be absorbed by the paper and not pass straight through (Fig. 14).

Envelopes are useful for estimating light contaminations, but although filter paper can absorb up to 100g/m² of most chargings it is found in practice that above 10 g/m² some of the liquid either flows off the edge of the envelope or passes through the filter paper before it is absorbed.

(b) THE FELT PAD

A piece of woollen "Fearnought" felt is arranged in a metal holder so that the exposed area of felt is 100 sq. cm. The felt gives a surface which is rougher than paper, has more rapid absorbing properties, and off which drops falling at an angle are less likely to bounce. The dyed charging also penetrates deeper into the pad than it does into paper and hence fading of the dye due to exposure to light and loss of dye due to volatility are reduced as compared with paper.

The present holder, which was designed for simplicity and speed of manufacture, consists of a flat piece of brass with one end curled over. The felt is cut 10 cm x 11 cm, and 1 cm of the length is forced under the curled edge of the holder; the opposite edge of the felt is then held down by a paper clip.

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Felt pads have been used as non-expendable stores i.e. the same pads have been used for several trials after extracting the dye from the pad and washing the holder. This has meant that they have not been very reliable in the areas of very light contamination. Also in these areas the small size of the pad gives too small a sampling area in relation to the scattered nature of the droplets. Pads, like envelopes, also tend to get displaced or turned over in the vicinity of a low burst bomb or near the crater of the bomb casing. With contaminations in excess of 200 g/m^2 , some of the charging passes through the pad.

Felt pads should therefore be used in the area where the contamination is expected to be in the range $1-100 \text{ g/m}^2$.

(c) TURF SAMPLING

The turf cutter consists of a circular metal cutter 3" in diameter to which is attached a long handle for convenience in cutting (Fig. 15). The cutter is forced into the contaminated turf with a rotary movement and then with the aid of a trowel a turf about 2" deep is lifted and transferred to a wide mouthed stoppered bottle, numbered to correspond with the position of the turf.

Turf cutting is resorted to in the areas of heavy contamination (over 50 g/m^2), particularly if the felt pads have been displaced, or if it is desired to take samples over a closer grid.

(d) THE PIE PLATE OR PETRI DISH

Enamel pie plates or petri dishes of known diameter have also been used to collect liquid contamination, the size being chosen to correspond with the degree of contamination expected i.e. a larger sampling area in the positions of lighter contamination.

These have been used in cases where pads could not be used, e.g. to estimate substances which could not be extracted easily from the pad or turf. Thus when it was required to estimate G itself and not the dye characteriser, the G would have hydrolysed to some extent on the pad. In other cases it was required to sample heavy contaminations on tarmac or concrete from which turves could not be cut.

In some cases the bottom of the petri dish is covered with a layer of absorbing solution, e.g. for GB it is covered with a film of cyclohexanol, to reduce evaporation before analysis.

In using petri dishes note must be taken of the screening action of the rim when the droplets arrive at an angle to the vertical.

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B. NOTES ON CRATER SAMPLING

It is sometimes desired to know the amount of charging left in a crater. For this purpose the loose earth is dug out and digging is continued till all the charging is removed. This is largely a matter of experience, but some guidance can be given. Thus, if the charging was dyed, digging should be continued until there is no colour left in the crater; if it has a strong smell, this should be made use of. In case of doubt it is always better to take too much rather than too little.

The soil dug out is well mixed, any large lumps broken up and any flints rejected. The thoroughly mixed earth is then quartered in the standard manner, the diagonally opposite quarters being weighed before being discarded. The mixing and quartering is repeated until the residue is a convenient size for analysis. This is also weighed, to give the proportion of sample to total crater contents.

The sample is then analysed in the appropriate manner for dye, nickel, or other characteriser.

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C. OPERATING DEVICES

1. FLOW CONTROL DEVICES

(a) The Critical Orifice

(i) General

When gas is drawn through an orifice by means of suction applied to one side, then, provided the pressure drop across the orifice has reached a critical value which is dependent on the geometry of the orifice, the mass flow of gas will remain constant irrespective of further increases in the pressure differential with increasing suction. The flow rate is proportional to the square of the diameter of the orifice. An internal diameter of 0.35 mm gives a flow rate of about 1 litre per minute, 0.5 mm diameter gives 2 litres per minute etc. For a hole in a flat plate the critical pressure differential is about half an atmosphere (35 cm of mercury), but it has been shown experimentally that a profiled orifice of venturi shape giving streamlined flow will act critically at a smaller pressure differential. Hence one pump can operate a greater number of samples through venturi type orifices than through orifices of the flat plate type.

Venturi orifices were originally constructed from polythene, with the inlet cone making an angle to the axis of $30 - 40^\circ$ and the outlet cone longer and with an angle of only 2° to the axis, experiments having shown this shape to be the best. When a few of these were produced, they were very satisfactory and acted critically as long as the pressure on the pump side was not more than $3/4$ atmospheric, i.e. a pressure differential of only $1/4$ atmosphere; but when produced in quantity the results were disappointing for 1 litre per minute flow, although by enlarging the hole they were suitable for use at 10 litres per minute.

A second type of critical orifice used consisted of a glass tube with one end constricted till the hole was of the correct diameter, but these also were unsuitable for mass production. The problem of producing large numbers of critical orifices with a reproducible flow-rate was finally solved by the introduction of the Veridia-disc orifice described below.

(ii) The Veridia Disc Critical Orifice

A length of capillary tubing can be used as an air flow regulator, but the flow rate is dependent on the pressure differential maintained by the pump. If however the length of the capillary is reduced to $1/16"$, it will act as a critical orifice providing the pressure on the pump side is less than half atmospheric. $1/16"$ thick discs of "Veridia" (precision internal diameter) tubing have been used as critical orifices and found very satisfactory.

The disc is forced into a piece of surgical rubber tubing of internal diameter about 2 mm less than the external diameter of the glass disc. On each side of the disc is placed a piece of plastic tubing (either fairly rigid polyvinyl chloride or polythene, according to the risk of attack by the vapour of the sampling solvent) with an outer diameter slightly less than that of the disc. This holds the disc at right angles to the axis, and acts as a spacing piece to allow the rubber to contract (Fig. 16). A length of at least $1/2"$ of PVC tube is found to be necessary to prevent leaks past the outside of the disc. The plastic tubing is held in place by either aluminium or glass tubing, which also serves to connect the critical orifice to (a) the sampling unit (b) the suction line

(b) The Ball and Tube Flowmeter

This is described with the Injector - see 3 (c) below.

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2. SAMPLE TIMING CONTROLS

(a) The Rotary Distributor

(i) The Bellows Operated Rotary Distributor

This was designed for operating at flow rates of at least 10 l/min. It consists of a flat plate with ten holes leading to ten sampling positions. A rotating hollow arm moves over the flat side of the plate to connect with each of the positions in turn. When suction is applied, this first compresses a bellows which moves the rotating arm to the first sampling position and when the pump is switched off the bellows expand and allow a ratchet mechanism to move the rotating arm to a blank position between the first two sampling positions. The connection between the rotating arm and the flat plate is not absolutely airtight, but since this is on the suction side of the critical orifice, it is unimportant unless the leak is so great that there is less than half an atmosphere pressure differential.

A lever at the back of the distributor allows it to be reset to No. 1 position by hand.

Since an air flow of about 10 l/min. is required to expand the bellows in a reasonable time, one of these rotaries is normally used to control several positions sampling at 1 l/min. When the rotary is controlling only one or two positions, a 5 or 10 l/min. critical orifice is inserted into the line between the pump and the rotary in order to increase the air flow and reduce the time required to switch the rotary to the next position.

In all cases the time for the rotary to operate must be checked and an interval of at least this period allowed between the successive samples.

(ii) The Schrader Valve Rotary Distributor

This apparatus is designed for taking up to six consecutive gas samples, using a single source of suction.

The six sampling lines connect via Schrader Valves to a plenum chamber which in turn is connected to the vacuum line.

The Schrader valves are opened sequentially by a cam driven by a rotary solenoid.

The distributor is used in conjunction with a remote control switch, which carries a pointer indicating which sampling line is in use.

This type of rotary distributor can be used only for flow rates below about 5 l/min. as above that rate the Schrader valves act as critical orifices themselves, and hence normally one distributor should control only one 1 l/min. sampling position.

When using this distributor, two separate electrical circuits are required, one for the pumps and one for the rotaries, and the gauge of cable used must be such that each distributor receives the correct 24 volts.

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(b) The Bomb Release Control for Evacuated Bottles

This control is an Air Ministry bomb release interval timer (Mickey Mouse pattern) such that when an electrical impulse is given, a lever arm snaps down.

An evacuated bottle fitted with a jet bent at right angles is placed alongside the bomb release so that the point of the jet protrudes through a hole in a metal frame and comes just below the lever arm.

The bottles are arranged in banks of four each with its own bomb release, so that by using four separate switches, four successive snap samples can be taken

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3. SUCTION DEVICES

(a) Pump for Large Scale Field Sampling (T.1 Pumps)

This is a series wound 24 volt D.C., 11.2 amps., 6,600 rpm, 1/4 h.p. motor attached to a diaphragm pump which is capable of pulling about 50 litres/min. of free air or of maintaining a vacuum of half an atmosphere when pulling 30 litres/min. of air through critical orifices.

In the field these pumps are used for sampling for up to 20 positions each at 1 l/min., the various positions being connected to the pump by lengths of piping and manifolds.

Some of these pumps have been modified to be operated at 110 volts D.C.

(b) Static Pump for Large Scale Sampling

This is a commercial pump operated by a 1 h.p., 220 volt A.C. motor at 1425 rpm and supplied by Messrs. Pulsometer of Reading. It is suitable for operating up to 50 positions at 1 l/min. in the laboratory, gas chamber or other permanent position.

(c) Miniature Pump for Individual Sampling

This is a 3.5 cc piston type toy Diesel engine converted to act as a pump, direct driven by a 24 volt D.C. 2,000 rpm shunt wound motor. These motors consume about 50 watts and the pumps pull 3 or 4 litres/min. of free air at about 2 litres/min. of air when maintaining a vacuum of over half an atmosphere.

They are intended to be used for sampling at individual points, but if necessary one pump (if in good condition) could be used for two positions each at 1 l/min.

(d) Vacuum Tanks

Vacuum tanks have proved useful at static positions e.g. the bursting chamber, where the flow rate for the number of samples required was greater than the capacity of the pump then available.

The vacuum tank can be any large airtight tank capable of withstanding the pressure - an empty bomb body was actually used. This is evacuated by the pump prior to the experiment and the sampling is controlled by a tap between the sampling points and the tank. A manometer is fitted to the tank to confirm that the sampling is terminated before the vacuum has been reduced to less than half an atmosphere, to ensure correct flow through the critical orifices.

(e) The Injector

The injector is self contained and, although it has been superseded by suction pumps for most layouts, it is still of value for remote or isolated sampling positions.

Two types of injector are available, one for complete control by hand, the other after a preliminary setting by hand is switched on and off electrically.

The injector operates on a similar principle to that of the Bunsen water pump and consists of the following parts. (Fig. 17):-

(i) The air bottle, a thin steel alloy cylinder is charged to a maximum pressure of 1,800 p.s.i. dry air, and should therefore be handled with care.

(ii) The main valve. This should be kept either fully opened or fully closed, in which cases the gland is self-sealing. At intermediate positions, air leakage and damage to the valve may occur.

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(iii) The reducing valve and gauge. When the injector is fully charged the gauge should show 120 atmospheres. When the pressure falls below 30 atm it is an indication that the injector will not continue to function much longer.

(iv) The injector unit is a stainless steel jet with a fine gauze filter, and discharges into - -

(v) The venturi tube and exit pipe.

(vi) The flowmeter usually fitted to the injector consists of a steel ball in a transparent plastic tube which is slightly tapered inside, and is calibrated at 10, 15, and 20 litres per minute. This flowmeter reads accurately only if the injector is placed in strictly horizontal position.

(vii) and (viii) The flexible inlet tube and adaptor

Notes (1) Injectors should be carried in boxes and, when removed from the box, should be lifted by holding the top of the reducing valve. They should never be handled by the thin tube connecting the main valve to the reducing valve, or by the flowmeter.

(2) Although the balls in the flowmeters are made of stainless steel, corrosion does occur and the balls often stick and have to be loosened by momentarily tilting the injector or by gently tapping the flowmeter tube.

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SECTION III

ANALYSIS OF THE SAMPLE

The analytical methods quoted below are as used for the samples from the most recent trials, but in some cases this is several years ago. (The date of last use is quoted after the heading in most cases, up to January 1955.)

In view of the changes in the technique of sampling - design of bubbler, flow rate used, etc. - some methods will require modification before being revived if the number of samples involved is appreciable. The volume of sampling solvent used will depend on the type of bubbler and on the flow rate, and as the efficiency of the sampling is dependent on all three of these as well as on the temperature and the time of sampling, the "slip"* should be checked before any modification is accepted.

In most cases typical calibration results are quoted. These are given as a guide to the sensitivity obtainable, and new calibrations should be carried out if the methods are revived or if new supplies of reagents are used.

It is considered that several of the methods could be improved, e.g. it is possible that where alcohol is used as sampling solvent it could be replaced by a less volatile solvent; in other cases titrimetric methods could be controlled amperometrically or replaced by more sensitive colorimetric methods. In these cases, however, the amount of recent use of the method has not justified the time required for its improvement.

*Slip is here taken as the amount in the second bubbler, expressed as a percentage of the amount in the first bubbler, when the sample is taken through two bubblers in series.

NOTE

Excluded from this memorandum, but included in P.M.19 are methods for:-

ANTIMONY (see also Ptn/1751(U2648))

CADMIUM

CHLORINE by mercuric nitrate titration

CHLOROCROTONALDEHYDE

ETHYL IODOACETATE (KSK)

HYDROGEN SULPHIDE

MAGNESIUM

OIL SMOKE

TITANIUM

ZINC (by visual estimation of turbidity with ferrocyanoide).

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A. ANALYTICAL INSTRUMENTS

1. Spekker Absorptiometer H760

This is a well known commercial instrument, supplied by Messrs. Hilger and Watts Ltd.

The Ilford filters ranging from "Spectrum violet 601" to Spectrum red 608" are now used with this instrument. However, some of the older methods quoted refer to the older type of "Spekker" and the glass filters No.1 Red to No.7 Dark Blue. The necessary modifications and recalibration should be made if the method has to be brought into use.

In order to simplify the analytical technique when dealing with large numbers of samples, the sampling bubbler is also used as the analytical vessel, and the reagents are added to the sample in "Situ". This means that the colour measurement has to cope with a very wide range of concentrations and to achieve maximum sensitivity a range of absorptiometer cells of varying size is used. Thus, pale colours are measured using cells with a path length of 3 cm and deeper colours in either 1 cm or 0.25 cm cells. In some methods, where the range of concentrations expected is extremely wide and the amount of reagent already added is sufficient to cope with this range, 0.25 mm cells have also been used, and the necessity of diluting and taking an aliquot part so avoided.

2. Unicam Spectrophotometer

This is also a well known commercial instrument, the Unicam S.P.350 Diffraction Grating Spectrophotometer, supplied by Messrs. Unicam Instruments Ltd. Solution cells ranging from 1 inch tubes to 0.25 cm cells are used with this instrument.

3. Fluorimeter

Since no commercial instrument with sufficient sensitivity was available, one was designed and produced at Porton (P.T.P.455), (Figs. 18 - 21).

The original fluorimeter was a single ended instrument, but later models employ the twin-beam principle and consist of:

Light Source:- A 12v, 24 watt Osram lamp having a single vertical spiral tungsten filament.

Detector System:- Two photomultipliers, one on each side of the lamp, are connected together with the final dynode load resistors, one of which is variable, in a bridge circuit. A galvanometer is joined between the final dynodes.

The photomultipliers are chosen with low dark current, high gain, and maximum response in the blue spectral region. 220 K 1 watt resistors are used in each dynode chain. The variable resistor is a 25 K Colvern "Helipot" fitted with a slow motion dial graduated in one thousand divisions, and is the final dynode resistor in the control photomultiplier circuit. The fixed load resistor in the final dynode of the test photomultiplier circuit is between 5 and 35 K and is chosen so that with no light on either photomultiplier and the variable resistor set at maximum the current is approximately balanced.

A Cambridge "spot" galvanometer; 1 microamp full scale deflection is used to indicate the null point.

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Test Cell:- An optical glass cell, internal dimensions 4.5 cm high, 3.5 cm long, and 1.5 cm wide, is used. Light enters the cell through a narrow face and the photomultiplier measuring the developed fluorescence is placed as near as possible to a wide face.

Filters (a) Woods glass filters are placed between test cell and light and between control photomultiplier and light.

(b) An Ilford 106 filter is inserted between the test cell and the photomultiplier to eliminate stray light reflected or refracted from the test solution.

(c) A neutral density wedge filter is placed between the control photomultiplier and the light source.

Power Pack:- A constant voltage transformer is used to supply:-

(a) A lightly stabilised 1400v, 4-5ma supply with a variable voltage control.

(b) A lamp transformer 12v, 2-3 amps.

Screening:- The test cell, photomultipliers and filters are screened to prevent the ingress of stray light and care should be taken each time the test cell is inserted that the metal cover is replaced in the correct position.

Light shutters are provided for stand-by use on control and test photomultipliers and on the test cell.

Use of the Instrument:- The instrument is switched on, allowed to warm up for 30 mins., the voltage on the photomultipliers adjusted to the standard value and the setting of the neutral density wedge checked as follows:-

A fluorescein or other standard fluorescent solution, having a fluorescence intensity equivalent to a standard reading in the range expected, is placed in the test cell. The variable load resistor ("helipot") is turned to the standard value and the wedge adjusted till zero current is recorded on the galvanometer.

A blank solution is placed in the test cell, and the "helipot" dial is rotated until a null point is indicated on the galvanometer and the number noted. The blank solution is removed, the test solution placed in the cell and the procedure repeated.

It is advisable to check blank and control readings at frequent intervals and make a small correction for drift due to temperature change.

4. Infra Red Gas Analyser

The I.R.G.A. is a commercial instrument supplied by Messrs. Grubb-Parsons. It consists essentially of:-

(i) A source of Infra Red radiation

(ii) A rotating chopper

(iii) Two parallel tubes, one of which contains air free from the gas to be estimated, whilst the sample is passed through the other at a slow steady rate.

(iv) A condenser consisting of a diaphragm and a fixed plate and containing the same concentration of the gas to be analysed on each side of the diaphragm.

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(v) An electrical measuring system.

An interrupted beam of infra red light is passed simultaneously down the two tubes and into the condenser. If the sample is "blank" the amount of radiation absorbed and heat produced is the same on both sides of the diaphragm, but if some of the gas is present this will absorb some of the radiation in the sample tube, so that the heating effect in the condenser will then be out of balance and the diaphragm will be displaced. This is measured electrically and the chopper enables an A.C. amplifier to be used.

The I.R.G.A. can be used for the estimation of carbon monoxide, carbon dioxide and for many hydrocarbons which absorb strongly at particular wavelengths in the infra red.

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B. METHODS OF ESTIMATION

1. ACETYLENE (1953)

USE

Acetylene has been used in trials requiring a true gas as an innocuous substitute.

PRINCIPLE OF THE METHOD

The acetylene solution is treated with an ammoniacal copper solution and the red copper acetylide (prevented from coagulating by the presence of gum ghatti) is measured in the Spekker Absorptionmeter.

COLLECTION OF THE SAMPLE

The acetylene is collected in bead bubblers charged with 20 ml of acetone. The bubblers are contained in a wooden box and packed round with solid carbon dioxide ("Cardice"). The sampling rate must not be more than 2 litres per minute; even at this rate the sampling time must not exceed 15 minutes, and it is essential to connect a second bubbler in series with the first, in order to estimate the "slip". At 100 cc per minute, however, the slip is negligible for short sampling periods.

REAGENTS

(i) 0.8 g of cuprous chloride A.R. is dissolved in 20 ml water and 9 ml of conc. ammonia solution A.R. (0.880). 7 g hydroxylamine hydrochloride dissolved in 30 ml of warm water are then added. After decolorisation, 20 ml of a 1% solution of gum ghatti is added and the mixture diluted to 100 ml in a graduated flask.

(ii) The gum ghatti solution is prepared by suspending 1 g of the gum in a muslin bag in 100 ml of water for 24 hours.

If it is desired to keep the mixed reagent for more than a few hours, a few strands of clean copper wire should be introduced, 2 or 3 ml of light petroleum floated on the surface and care taken to avoid undue shaking.

ANALYTICAL METHOD

Each bubbler is stored in the "Cardice" until ready for analysis and as soon as the analysis is started it is carried through as rapidly as possible. All flasks, cylinders, pipettes and the water and acetone used for dilution are cooled in an ice bath until ready for use.

If the sampling rate was 100 cc per minute, so that there has not been any loss of acetone, the sample is poured into a cylinder, and 10 ml (i.e. half the sample) pipetted out into 10 ml of ice-cold acetone in another cylinder. The mixture is diluted to 40 ml with cold water, 2 ml reagent added and mixed with a plunger stirring rod and the mixture allowed to stand for 5 mins. in a water bath at 20-25°C for the colour to develop. The colour is measured in the Spekker using 4 cm or smaller cells as appropriate with the OB1 dark blue screens and distilled water in the reference cell. If the colour is too dark to measure on the 0.25 cm cell a repeat on a smaller aliquot must be carried out at once; with practice it is possible to tell if this will be necessary as soon as the reagent has been added so that a repeat can be started before any acetylene has been lost from the sample.

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For samples taken at 1 or 2 litres per minute, the contents of the first bubbler are poured into a measuring cylinder, and the contents of the second bubbler used to wash out the first; this is washed with a little acetone and the washings added to the sample until the volume is 40 ml. The solution is mixed with a plunger stirrer, and an aliquot of not more than 20 ml taken and diluted to 20 ml if necessary with acetone, then to 40 ml with water and the estimation carried out as above.

Blanks should be carried out on 20 ml acetone.

CALIBRATION

A 10 ml gas sampling tube whose volume is accurately known is filled with acetylene from a cylinder and the temperature and barometric pressure noted. This is then connected to a bead bubbler containing 40 ml acetone cooled in "Cardice" and the tap next to the bubbler opened. The bubbler is then connected to the suction and the other tap opened and a very slow stream of air (not more than 100 cc per min.) drawn through until all the acetylene has been absorbed in the acetone.

Several small aliquots are then taken from this solution and the acetylene estimated as above, the weight of acetylene in the aliquots being calculated from the volume of the sample tube corrected for temperature and pressure and for the aliquot taken.

Typical results are as follow:-

Acetylene mg	0.0	0.38	0.76	1.14	1.52
Spekker Reading	0.01	0.63	1.25	1.88	2.48

(The higher Spekker readings are measured on the smaller size cells and multiplied by the appropriate factor)

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2. AMMONIA (1954)

USE

Ammonia has been estimated in gun fumes in tanks and confined spaces, pill boxes etc.

PRINCIPLE OF THE METHOD

The development of the well known yellow colour with Nessler's reagent and its measurement on the Spekker.

COLLECTION OF THE SAMPLE

Ammonia is collected in miniature bubblers charged with 5 ml 0.01N. Hydrochloric acid, operated at 1 litre per min., or in evacuated Winchester bottles. Slip can be neglected for samples up to 30 mins. at 1 litre/min.

REAGENTS

(i) 35 g potassium iodide A.R. and 13 g mercuric chloride are added to 800 ml water, heated to boiling and stirred till dissolved. A cold saturated solution of mercuric chloride is then added dropwise until the red periodide of mercury just begins to be permanent. 160 g of solid potassium hydroxide A.R. are added and the solution diluted to 1 litre. A little of the saturated mercuric chloride solution is then added and the precipitate allowed to settle.

The reagent should be prepared in advance as it improves on keeping. It should be kept in the dark.

(ii) 1% gum ghatti solution.

ANALYTICAL METHOD

A calibration curve should be prepared at the same time as the samples are examined, using a standard solution of ammonium chloride.

If collected in miniature bubblers, the sample is diluted to the 25 ml mark with mixed reagent consisting of 20 parts water, 1 part Nessler reagent, and 1 part gum ghatti solution, stirred and allowed to stand 5 mins., the colour measured on the Spekker, using the Spectrum Violet 601 screens and either the 3 cm or the 1 cm cells. If the sample is expected to be very high (over 200 μ g), an aliquot should be taken before adding the reagent.

If the sample is collected in Winchesters, 25 ml distilled water are added, the mixture shaken round well and poured into a 50 ml cylinder. The bottle is washed out with more water and the washings added to the cylinder, the volume being finally made up to the 50 ml mark. 2 ml Nessler reagent and 2 ml gum ghatti solution are added, the mixture stirred and the colour measured on the Spekker. This, of course, will require a different calibration curve.

CALIBRATION

By the bubbler method, typical results are:-

μ g NH_3	0.0	10.3	20.	30.	40.	50.
Spekker reading	0.05	0.10	0.31	0.47	0.62	0.77

SECRET

3. ANILINE (1954)

USE

Aniline has been used as a substitute, particularly for annulus and other evaporation trials.

PRINCIPLE OF THE METHOD

Aniline reacts with p-dimethylaninobenzaldehyde to give a yellow colour

COLLECTION OF THE SAMPLE

The vapour is collected in miniature bubblers charged with 2 ml of 50% acetic acid. "Slip" at 1 l/min is about 3% for sampling periods of 30 mins. and at a temperature of 65°F.

REAGENTS

- (i) 50% Acetic Acid A.R.
- (ii) 0.1% solution of p-dimethylaninobenzaldehyde in 50% acetic acid.

ANALYTICAL METHOD

The bubbler contents are made up to the 25 ml mark with the p-dimethylaminobenzaldehyde reagent, stirred with a glass plunger stirrer, allowed to stand for 10 minutes, and the colour read in the "Spekker" using Spectrum Violet 601 screens and the appropriate cell (3 cm, 1 cm, 0.25 cm or 0.25 mm) and comparing against a blank made in the same way.

TYPICAL CALIBRATION CURVES

The aniline solution for calibration is prepared by dissolving 0.1392 g aniline hydrochloride in 1 litre of 50% acetic acid and diluting 10 ml of this solution to 100 ml with more 50% acetic acid.

Aniline µg	10	20	30	40	50	60	120
Reading:							
3 cm cell	0.21	0.395	0.56	0.73	0.85	0.945	0.
1 cm cell			0.21			0.385	0.705
Aniline µg	120	180	240	360	480		720
Reading:							
1 cm cell	0.705	0.96					
0.25 cm cell	0.205		0.38	0.54	0.685		0.94
Aniline µg	1200	2400	3600	4800	6000	7200	
Reading							
0.25 mm cell	0.20	0.39	0.525	0.655	0.79	0.90	

If preferred, instead of using the 0.25 mm cell, a 1 ml aliquot can be removed from the bubbler, diluted to 25 ml with more p-dimethylaninobenzaldehyde reagent and either the 1 cm or the 0.25 cm cell used.

SECRET

4. ARSENIC (pre 1946)

PRINCIPLE OF THE METHOD

The action of nascent hydrogen on an arsenite solution liberates arsine, which is oxidised to arsenic acid by iodine. The arsenic acid is then estimated by means of the intense blue colour produced by reduction of an arseno-molybdate solution with stannous chloride.

COLLECTION OF THE SAMPLE

- (i) Vapours - Methyl dichloro and difluoroarsine, Ethyl dichloroarsine, collected in bead bubblers containing 15 ml 5% NaOH.
- (ii) Mixed vapour and particulate - Lewisite, phenyl dichloroarsine collected on (Whatman No.1) filters backed by a bead bubbler 15 ml 5% NaOH.
- (iii) Particulate - DA, DA acid, DA oxide, DA sulphide, DC, DM, collected on filters (Whatman No.1)
- (iv) Solid (gross) - DC, collected on envelopes, and dug out from craters.
- (v) Liquid - BBC, H, LS, HN₂ containing DA, DC or TA, collected on sampling envelopes, and dug out from craters.

REAGENTS

- (i) Conc. HNO₃ and conc. H₂SO₄
- (ii) 50% aqueous KI.
- (iii) 40% stannous chloride in conc. HCl.
- (iv) Arsenic-free zinc pellets.
- (v) N/50 iodine solution.
- (vi) N/2 sodium bicarbonate solution.
- (vii) 5% sodium metabisulphite solution.
- (viii) Sulphuric-molybdate solution. Made by mixing equal volumes of 13 N.H₂SO₄ (accurately standardised) and 9.5% sodium molybdate (Na₂MoO₄ · 2H₂O).
- (ix) Dilute stannous chloride solution (0.2%). Prepared by diluting with water the 40% solution (1/200) as required; this solution must be freshly prepared, at least once every day.

All reagents should be free from arsenic or phosphorus. Only freshly prepared solutions of sodium bicarbonate and sodium metabisulphite should be used.

ANALYTICAL METHOD

The method may be divided into four stages:-

- (i) Destruction of organic matter and oxidation to arsenic acid.
- (ii) Reduction to arsenious acid.
- (iii) Evolution and absorption of arsine.
- (iv) Colour development.

SECRET

(1) Destruction of organic matter and oxidation to arsenic acid. The sample is transferred to a 200 ml Kjeldahl flask, sufficient conc. HNO_3 added to cover the sample, and sufficient conc. H_2SO_4 to leave

1 - 2 ml after nitration is completed (a 5.5 cm Whatman No. 1 filter needs about 2 ml but an envelope 4 - 5 ml). The flask is clamped on the heater, the shaker (fig. 22) set going if there is any tendency to bump or froth, and heating continued until white fumes of SO_3 are evolved. If the liquid is black owing to charring, more HNO_3 is added by means of a dropping bottle and the liquid evaporated to SO_3 fumes. The process is repeated if necessary till no carbonaceous matter remains.

(For earth samples, the substance is gently heated (and shaken if necessary) without the addition of H_2SO_4 until all frothing ceases, care being taken not to allow the contents of the flask to become dry. Sufficient H_2SO_4 is then added to keep the contents liquid, the sample charred and HNO_3 added as above. Complete destruction of organic matter has occurred when SO_3 is evolved and no further charring occurs).

The mixture is allowed to cool somewhat, 10 ml water are added and the liquid again evaporated (shaking if required) to SO_3 fumes (this removes excess HNO_3), and finally allowed to cool.

(ii) Reduction to arsenious acid. The solution in the Kjeldahl flask is diluted to about 90 ml with water, 1 ml 50% KI and 1 ml 40% stannous chloride are added and the mixture is just brought to the boil, then cooled to room temperature.

(iii) Evolution and absorption of arsine. The arsenite solution is made up to a known volume, and an aliquot portion containing not more than 0.1 mg. arsenic transferred to a Gutzeit pot (Fig. 23), (Note: the pot need not be of standard dimensions since rate of arsine evolution is not important). 2 ml conc. H_2SO_4 , 10 ml conc. HCl and 1 ml 40% stannous chloride are introduced into the pot, water added to about the 50 ml mark, and the mixture allowed to cool.

The pot is now fitted up as follows:- The top is closed with a rubber bung into which passes a tube about 1.5 cm wide and 12 cm long and with a constriction near the middle. The upper part is packed loosely with glass wool soaked in lead acetate so as to absorb any hydrogen sulphide. The top of the tube is fitted with a rubber bung from which emerges a capillary tube (4 mm external and 0.5 mm internal) bent with a double right angle so that it passes into a narrow absorption tube standing upright by the side of the pot; the narrow tube is widened at the top in order to prevent loss by splashing, and is preferably graduated at 10 ml. The capillary should be in contact with the bottom of the tube.

5 ml N/50 iodine and 2 ml N/2 sodium bicarbonate are placed in the side tube, 5 g zinc shot are put into the pot, and the stoppers pressed home to prevent gas leak. Under these conditions evolution of arsine is complete in 30 minutes.

SECRET

(iv) Colour Development.

2 ml sulphuric-molybdate solution are added to the side tube and mixed, and 0.1 ml sodium metabisulphite solution then added and mixed, 1 ml 0.2% stannous chloride is added and again mixed. The blue colour (which develops after 5 minutes) is measured on a Spekker absorptionmeter using the red filters.

A blank determination is performed with each batch of estimations, using all the reagents and going through the whole process, and the blank figure is subtracted from the result.

CALIBRATION

A calibration curve relating Spekker readings to concentrations of arsenic is prepared by taking standard arsenite solutions and submitting them to the arsine evolution technique described above. A blank is carried out on all solutions at the same time, the reading obtained subtracted from those given by the standard solutions, and the resulting figures plotted against corresponding arsenic concentrations.

Typical calibration:-

mg Arsenic	0.0	0.02	0.04	0.06	0.08
Spekker Reading	0.10	0.34	0.59	0.84	1.09
Difference		0.24	0.49	0.74	0.99

It is necessary to check the calibration curve for each new sulphuric-molybdate solution, and if any discrepancy is noted a new curve must be prepared.

Notes:

(1) Transferring the sample to the Kjeldahl flask

- (a) Sampling Envelopes. The edge of the paper is cut round with a sharp knife, the paper screwed up and placed in the flask.
- (b) Earth samples. A weighed portion of not more than 5 grams is analysed.

(2) Separation of Organic from Inorganic Arsenic

- (a) DM and DC. The filter paper is placed in a beaker and washed 3 times with about 10 ml of warm carbon tetrachloride previously freed from all traces of phosgene by refluxing over solid NaOH and distilling. The washings, which contain the organic arsenic, are filtered through Whatman No. 1 filter paper into a Kjeldahl flask. The residue in the filter, plus the original paper, contain the inorganic arsenic.

Concentrated HNO_3 tends to oxidise a portion of the carbon tetrachloride to chloroform and phosgene. These react with the arsenical, forming the volatile arsenic trichloride, and resulting in loss of arsenic. It is therefore necessary to proceed as follows:-

To the carbon tetrachloride extract, 10 ml water and 3 ml chromic acid solution are added. The latter is made by dissolving 35 g CrO_3 in 100 ml water and adding 1100 ml conc. H_2SO_4 . The flask and contents are shaken well. The carbon tetrachloride is evaporated off on a Water bath, and the "Kjeldahl" process proceeded with. (No more sulphuric acid need be added).

- (b) DM. Separation as above, except that acetone must be used. The acetone must be removed by evaporation before nitration, but in view of the lower volatility of DM as compared with DC, this may be done without preliminary oxidation by chromic acid. The filter containing the inorganic fraction is freed from acetone by exposure to a gentle stream of air.

SECRET

(3) Care of Samples

Even fine particles of arsenical may be dislodged from the paper by rough handling; the filter should therefore be kept flat in the "nests" provided for the purpose.

If the sample has to be kept for some time before analysis, it should be placed in a dish under concentrated nitric acid, acetone or carbon tetrachloride as the case may be to prevent evaporation of the arsenical, and covered with a watch-glass.

(4) Sensitisation of Zinc

All zinc must be sensitised before use by treating for a few minutes with dilute HCl , then washing with distilled water. The sensitised zinc should be kept under distilled water until required for use.

(5) Lewisite

In the case of Lewisite samples, collected on filters backed by bead bubblers containing 15 ml 5% NaOH , it is not necessary to carry out stage 1 of the analytical method quite so fully.

The bubbler sample (for vapour), the filter plus 15 ml 5% NaOH (for liquid), or the filter and bubbler sample together (for total) are transferred to a Kjeldahl flask containing 2.5 ml conc. H_2SO_4 . To this is added 2 or 3 ml of conc. HNO_3 and the usual wet oxidation carried out. After complete removal of all nitric acid, 80 ml of water are added, then 1 ml 50% KI and 1 ml 40% SnCl_2 . The solution is brought to the boil, cooled immediately, and made up to 100 ml. A suitable aliquot containing not more than 0.1 mg arsenic is taken for analysis as described above for the evolution and absorption of arsine. If necessary more sulphuric acid must be added in the evolution stage. Of the 2.5 ml of H_2SO_4 added originally 0.5 ml will have been required to neutralise the 15 ml 5% NaOH , leaving 2 ml in the 100 ml from which the aliquot has been taken, and the aliquot itself should contain at least 2 ml conc. H_2SO_4 .

A more rapid method has also been used for Lewisite as follows:

Principle of the Method

The lewisite is converted to sodium arsenite which is then titrated against standard iodine.

Collection of the Sample

The samples are collected on No. 1 Whatman filter paper backed by a bubbler containing 5% sodium hydroxide solution.

Reagents

- (i) Standard sulphuric acid. This must be such that 5 ml + 0.1 ml just acidifies the amount of solution used in the bubblers.
- (ii) 0.002N Iodine
- (iii) 1% starch (freshly prepared)
- (iv) Sodium bicarbonate (solid)

Analytical Method

Analysis should be carried out as soon as possible after sampling. 5 ml of sulphuric acid are added to the bubbler and the contents poured into a small conical flask, to which the filter paper is added. 1 ml of starch solution is added and about 1 g of sodium bicarbonate dissolved in the solution, which is then titrated with iodine from a micro-burette.

SECRET

A blank is run simultaneously and is titrated to the same depth of colour. With large samples the colour match is not good but the error introduced is not serious.

The accuracy of the method is $\pm 10\%$ on dosages (Ct) of 20 ng.min/m^3 of lewisite vapour (and upwards).

SECRET

5. ARSINE (pre 1946)

PRINCIPLE OF THE METHOD

Two methods are employed. In one, arsine precipitates silver from silver nitrate, and the precipitate is dissolved in nitric acid and estimated by the Volhard method. In the other method arsine is oxidised by iodine, and excess of the latter is titrated with sodium thiosulphate.

COLLECTION OF SAMPLE

Arsine is collected in bead bubblers containing 3% silver nitrate, or in evacuated bottles.

REAGENTS

- (i) Conc. HNO_3
- (ii) N/50 KONS
- (iii) Ferric Alum
- (iv) N/50 iodine
- (v) N/50 sodium arsenite

ANALYTICAL METHOD

(1) Bubblers. A Gooch crucible is prepared with a thin pad of asbestos and the contents of the bubbler are poured through it via the side arm of the bubbler.

The bubbler is washed two or three times with distilled water and the washings poured through the gooch crucible. A little of the final washing is poured into dilute HCl and if a precipitate of silver chloride is observed the bubbler is again washed. This procedure is repeated until no precipitation of silver chloride occurs.

The plate and pad of the gooch are next placed in a beaker flask and the gooch washed with conc. HNO_3 to remove all the silver adhering to the sides. The HNO_3 is run into the crucible from a dripper, the gooch being held over the beaker flask so that the acid runs in on to the pad and plate.

The contents of the flask are swirled round to break up the asbestos pad and dissolve all the silver on it.

Next the bubbler is about one-fourth filled with conc. HNO_3 shaken up and the acid poured into the beaker flask via the side arm. Finally the bubbler is washed two or three times with distilled water to remove the last traces of dissolved silver.

The resulting solution of AgNO_3 in the beaker flask is titrated against N/50 potassium thiocyanate using a few drops of ferric alum solution as an internal indicator, the end point occurring when a very slight pink coloration persists after shaking.

N.B. The pad of asbestos in the gooch should be as thin as is practicable since a large quantity of asbestos in the final solution obscures the end point.

The bulk of the final solution should be kept as low as possible for the same reason.

1 ml N/50 KONS \equiv 0.26 mg AsH_3 .

SECRET

(ii) Bottles The analysis is carried out in the bottle. About 5 g sodium bicarbonate are introduced into the bottle and 25 ml N/50 iodine are run in from a pipette. The contents are swirled around and diluted with water, and after standing a few minutes the resultant liquid is titrated against N/50 sodium arsenite solution, using starch solution as indicator. The difference between 25 ml and the amount of arsenite used gives the quantity of iodine absorbed by the arsine.

The volume of the bottle is noted.

1 ml N/50 iodine \equiv 0.195 mg AsH_3

SECRET

6. BROMOBENZYL CYANIDE (pre 1946)

PRINCIPLE OF THE METHOD

Bromobenzyl cyanide in alkaline alcoholic solution gives a purple colour with 4,6-dichloro-1,3-dinitrobenzene.

COLLECTION OF THE SAMPLE

The sample is taken at 10 l/min. in bead bubblers charged with 15 ml of absolute alcohol.

REAGENTS

- (i) Absolute alcohol
- (ii) 2% sodium hydroxide in distilled water
- (iii) 4% solution of 4,6-dichloro 1,3-dinitrobenzene in dioxan.
This solution is stable for at least 4 weeks.

The 4,6-dichloro 1,3-dinitrobenzene is prepared by dissolving 34 g potassium nitrate in 170 g conc. sulphuric acid in a glass stoppered flask and cooling to room temperature. 25 g m-dichlorobenzene are then added in small quantities with vigorous shaking, the temperature being allowed to rise to 60-80°C. After all the dichlorobenzene has been added, the mixture is allowed to stand for 1 hour and is then poured into about 1 litre of water with rapid stirring. The solid is collected on a large Buchner funnel and pressed to remove liquid impurities. It is recrystallised from 200 ml boiling alcohol, dissolved in 100 ml chloroform and precipitated by the addition of 300-400 ml 60-80°C petroleum ether. Yield about 16 g pale yellow needles. M.pt. 103°C, insoluble in water, sparingly soluble in petroleum, and about 2% soluble in cold alcohol.

ANALYTICAL METHOD

An aliquot containing not more than 0.25 mg BBO is placed in a large test tube and alcohol added to total 20 ml. 1 ml of the 4% 4,6-dichloro 1,3-dinitrobenzene solution in dioxan is added followed by 10 ml of the sodium hydroxide solution and mixed. The colour intensity is measured in the Spekker between 10 and 20 mins. after adding the alkali using the No. 5 green screens and the 4 cm cells. If the solution is allowed to stand, fine crystals form, which are not readily dissolved out, hence special care should be taken to rinse the Spekker cell thoroughly with alcohol after each series of readings.

Dilute solutions of BBO in alcohol are unstable and all samples should be analysed within 2 days.

Note:

This colour is given by benzyl cyanide as well as by phenyl-bromoacetonitrile. 0.1 mg benzyl cyanide gives the same reading as 0.07 mg PBAN. The proportion of PBAN in commercial BBO is not constant and the product also contains some benzyl cyanide.

For initial clouds, when the constituents of the vapour will be in the same proportion as in the charging, the results can be reported in terms of charging (i.e. production BBO), but for persistent samples, the constituent of main interest, namely PBAN, is less volatile and the results will be more accurate if reported on a PBAN basis.

SECRET

TYPICAL CALIBRATIONS

mg BBO (70% PBAN)	0.0	0.01	0.02	0.06	0.10	0.14
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Spekker reading	0.05	0.15	0.25	0.58	0.92	1.21
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mg Pure PBAN	0.04	0.10
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Spekker reading	0.45	1.00
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Note

Since alcohol is used as the sampling solvent, the method given above is suitable only for short period sampling.

A less sensitive method in which alcoholic potash is the solvent is described in FM.19.

SECRET

7. CARBON MONOXIDE

USE

Carbon monoxide has been used as a substitute in cases where a true gas unaffected by atmospheric humidity was required. It has also been estimated in gun turrets and other closed compartments.

(a) By Use of the Infra Red Gas Analyser (1955)

PRINCIPLE OF THE METHOD

Carbon monoxide absorbs infra red radiation and the heating effect produced is measured on the machine.

COLLECTION OF THE SAMPLE

No suitable absorbent is available for carbon monoxide. It is collected in balloons, evacuated bottles, or by water displacement from bottles or aspirators, etc.

For trials to determine the effect of gun fumes in a turret, pill box, etc. where the main purpose of the trial is to compare two guns or two types of shell, it was desired to know the concentration in the shell case. Rubber caps have been made to fit over the cases from 17 pr and 20 pr shell, these caps being fitted with a tube closed by a screw clip through which the sample can be withdrawn for analysis when required. The shell case is caught and capped as it is ejected from the gun, so that capping takes place within 3 seconds of firing. This sampling technique is never used alone, but to confirm differences which might be detected by analysis of the concentration in the turret as a whole.

REAGENTS

None.

ANALYTICAL METHOD

The sample is passed through a drying tower and an absorption tube to remove carbon dioxide and then through the I.R.G.A. at a speed not exceeding 2 litres per minute, and the reading noted when this has become steady.

With balloons the natural compression of the rubber will usually force the sample through the I.R.G.A. at about the correct rate, whilst from bottles etc., the sample is forced into the machine by allowing water to run into the bottle at this speed.

CALIBRATION

A tube with two taps with a measured volume of about 1 ml between the taps (including the bore of each tap) is filled with carbon monoxide from a cylinder, allowing sufficient time to sweep all the air from the tube, and finally turning off the tap next to the cylinder before turning off the other tap to ensure that the pressure is atmospheric. The ends of the tube beyond the taps are then purged by filling with water from a tube drawn out to a fine jet, after which the carbon monoxide is drawn into an evacuated bottle of known volume. This concentration is then passed through the I.R.G.A. in the same way as the samples. A correction is made for the temperature and atmospheric pressure when calculating the weight of carbon monoxide in the standard.

Typical results:

% CO (Wt/vol)	0.0	0.02	0.04	0.06
Reading	5.8	13.8	21.6	30.5

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CARBON MONOXIDE (cont'd)

(b) Iodine pentoxide method (1953)

PRINCIPLE OF THE METHOD

Carbon monoxide reduces iodine pentoxide to iodine which is titrated with sodium thiosulphate.

COLLECTION OF THE SAMPLE

See (a) above.

REAGENTS

- (i) Chromic-sulphuric acid. 35 g chromic acid dissolved in 100 ml water and 1100 ml conc. H_2SO_4 .
- (ii) 1 - 2% KI.

METHOD

Water is supplied from a constant head apparatus to a series of 6 tubes, each of which supplies one train, the rate of flow of water being controlled by screw clips. To each tube is attached a long glass tube in a rubber bung which fits the sample bottle, the outlet from the bottle being a shorter glass tube also fixed in the bung.

The sample displaced by the water passes through a train of reagents in the following order (fig. 24):-

- (i) Small Dreschel bottle containing approximately 50 ml chromic acid - sulphuric acid; this removes SO_2 and unsaturated hydrocarbons.
- (ii) Small bead bubbler containing 20 - 30 ml conc. H_2SO_4 , heated to approximately $100^\circ C$. This removes traces of impurity not removed by the first bubbler.
- (iii) Small tube of caustic soda flakes to remove acid spray.
- (iv) P_2O_5 U-tube to ensure complete drying.
- (v) Iodine pentoxide U-tube heated to $160^\circ C$. This tube is filled with alternate layers of glass wool and I_2O_5 , the latter being graded 30 - 60 mesh.
- (vi) Bubbler containing 1 - 2% KI to absorb liberated iodine.

The procedure is as follows:-

- (i) Whilst they are heating a stream of air is drawn through the trains by suction from the bubbler end, to remove any impurities or iodine left in the apparatus.
- (ii) The bottle is attached to the water supply and train by quickly removing the bung and replacing with the fitted bung provided.
- (iii) By water displacement, the sample is slowly passed through the train (roughly 1 litre per 30 minutes) until the KI bubbler is a deep brown (i.e. is easily titrated with N/50 thio.).

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- (iv) The sample is disconnected and air drawn through the train for a further 10 minutes. If the sample is heavy, care should be taken to ensure that all the liberated iodine passes into the bubbler. It is sometimes necessary to warm slightly the outlet end of the I_2O_5 tube.
- (v) The bubbler is disconnected at the inlet end to prevent sucking back, and the contents washed out into a flask, and titrated with N/50 thio-sulphate, using starch as indicator.
- (vi) Pure air is drawn through the train for the same time and at the same rate as that used for the sample, the iodine liberated estimated and a correction made for this "blank".
- (vii) The volume of water in the bottle (= volume of sample taken) is measured (to nearest 10 ml)

1 cc N/50 thiosulphate \equiv 1.12 cc CO.

Notes:

- (1) When a fresh I_2O_5 tube is prepared, it is essential to check it before use, by passing a known CO concentration through the train in the same way as a sample, to ensure that the full amount, of iodine is released.
- (2) The I_2O_5 must be prepared with chloric acid, not HNO_3 .

(c) Use of the R.A.E. Detector

Where an approximate result is sufficient and particularly in comparison trials, the R.A.E. carbon monoxide indicator is used.

This indicator, which was developed at Farnborough, is very readily portable and has the great advantage of giving an immediate result.

The carbon monoxide is absorbed by silica gel, which has been impregnated with potassium pallado sulphite, and which changes colour from canary yellow to sepia. The length of the stain is proportional to the amount of carbon monoxide.

SECRET

8. CHLORIDE

USE

A non-specific method for the analysis of phosgene, chlorosulphonic acid etc.

PRINCIPLE OF THE METHOD

The chloride is titrated with silver nitrate, the end point being indicated by means of a galvanometer and a reference electrode constructed to give the same EMF as the titration solution at the end point (Pinkhoff Electrode).

APPARATUS AND ELECTRODES

The apparatus consists of two cells containing the two electrodes, joined by an ungreased tap. The larger of the two cells is the titration cell; this is fitted with a mechanically driven propellor type stirrer, and has a side arm for filling and a drain tap. The burette is drawn out so that the jet is kept below the level of the titration fluid (Fig. 25).

The electrodes consist of thick silver wire of 0.5 - 1.5 mm diameter and 1.2 - 2.0 cm length. They are mounted in the ends of glass tubes by means of Faraday or Picein wax, the latter being preferable. Copper wires soldered to the upper ends of the electrodes are led out to the galvanometer. The wax seal must be water-tight as any leakage will give rise to a spurious EMF. The electrodes are prepared by polishing or scraping with a clean sharp knife; once cleaned they should be kept immersed in their respective cell fluids and never allowed to become dry. Loss of sensitivity is cured by recleaning the titration cell electrode; wiping with filter paper is usually sufficient.

The cell should always be tested before use by titrating a standard chloride solution. With new electrodes several titrations may have to be done before the electrodes "settle down".

In order to protect the electrodes from heavy polarising currents, when the titration is far from the end point, it is desirable to mount a high (ca 300,000 ohm) resistance in series with the electrodes and the galvanometer and to use a shorting switch to allow full sensitivity for the final stage of the titration.

The Cambridge Spot Galvanometer identical with that used with the "Spekker" is very suitable for use with this apparatus.

REAGENTS

(i) Reference Cell Solution 10 g A.R. potassium nitrate and 14 g sodium oxalate are dissolved in distilled water 10 ml of Normal silver nitrate solution are added and made up to 1 litre with distilled water. This solution should be kept in a dark bottle and should be well shaken before pouring into the reference cell so that some of the precipitate is included.

(ii) Silver nitrate The silver nitrate solutions may be of any strength from 0.1N to 0.001N.

(iii) The sample should be in solution in either dilute acetic acid or in 0.25N potassium nitrate solution made by dissolving 25 g KNO_3 in distilled water up to 1 litre.

The titration cell electrode should always be kept immersed in potassium nitrate solution when not in use

METHOD (PR2664)

The solution containing the chloride is poured into the titration cell, acidified with dilute acetic acid if necessary and the volume made up to cover the electrode. It is desirable always to use approximately the same volume of liquid in the cell.

SECRET

The stirrer is started, the series resistance switched into circuit, and standard silver nitrate solution added until the galvanometer spot is approaching zero. The shorting switch is then used to cut out the resistance and the titration continued until opening and closing the shorting switch has no effect on the galvanometer spot. This point may not exactly coincide with the galvanometer zero owing to the existence of occasional small spurious EMF's in the circuit.

The "blank" is best determined by titrating various volumes of standard chloride added to the solution used and extrapolating the graph back to zero chloride.

SECRET

9. CHLORINE

USE

Chlorine has been used to test respirators for leakage, etc.

(a) By absorption in arsenite solution and potentiometric titration (1954)

PRINCIPLE OF THE METHOD

The chlorine is absorbed in sodium arsenite solution so that it will all be converted to chloride without any hypochlorite formation, and the resulting solution is then titrated potentiometrically as described for chloride (see 8 above).

COLLECTION OF THE SAMPLE

The sample is collected in bubblers charged with 0.02 N sodium arsenite solution.

This method was used where it was desired to take the samples at a maximum respiratory flow, i.e. an intermittent flow of 50 litres/min., and hence it was necessary to use the large sintered glass bubblers. For high concentrations two bubblers were used in series and the first bubbler was charged with up to 180 ml of the solution according to the concentration expected, the second bubbler being charged with 60 ml.

For 1 litre/min. sampling and lower concentrations miniature bubblers charged with 4 ml of the arsenite solution are used.

REAGENTS

0.99 g arsenic trioxide dissolved by warming in a little concentrated sodium hydroxide solution is washed into a graduated litre flask. One drop of phenolphthalein is added and the solution titrated with dilute sulphuric acid till just acid. 4 g of sodium bicarbonate dissolved in 500 ml of water are now added (and if necessary to maintain its acidity to phenolphthalein, another drop or two of the sulphuric acid) and then diluted to 1 litre.

ANALYTICAL METHOD

The bubbler contents with the addition of a little dilute acetic acid are titrated potentiometrically with silver nitrate as described above. For large volumes of solution it may be necessary to carry out the titration in instalments.

SECRET

CHLORINE (cont'd)

(b) o-Tolidine method (1951)

PRINCIPLE OF THE METHOD

"Available" chlorine gives a yellow colour with o-tolidine.

COLLECTION OF THE SAMPLE

The sample is collected in bead bubblers charged with 15 ml of 0.002 N sodium hydroxide solution at a sampling rate not exceeding 2 litres/min. and with a "slip" bubbler in series.

REAGENTS

- (i) 0.002 N.NaOH
- (ii) o-Tolidine (B.D.H. reagent)
- (iii) Standard chlorine solution. Chlorine is bubbled through water for a short time and the resulting solution standardized by taking an aliquot and titrating the iodine liberated from potassium iodide. Another aliquot is then suitably diluted to about 2 μg Cl_2 per ml with 0.002 N sodium hydroxide and used for the calibration curve.

ANALYTICAL METHOD

Within not more than 1 hour of sampling the bubbler is emptied into a measuring cylinder, the contents of the second bubbler used to wash out the first and the sample and washings made up to 40 ml. 0.5 ml of o-tolidine reagent is now added, mixed and allowed to stand for 3 minutes, and the colour then measured on the Spekter using 4 cm cells and the No.7 dark blue screens.

TYPICAL CALIBRATION CURVE

μg Chlorine	0.0	4.2	8.4	12.6	16.8	21.0
Spekter reading	0	0.11	0.235	0.375	0.475	0.57

Note

A method using o-dianisidine for the determination of chlorine has been developed by McEwen and Grant, Canadian Journal of Technology 30, 66, 1952.

SECRET

CHLORINE (cont'd)

(c) Rapid method using the "chlorimeter" (1951)

PRINCIPLE OF THE METHOD

The air sample is aspirated by means of a pump of known capacity through a solution of sodium arsenite, potassium iodide and starch. When all the arsenite has been converted to arsenate, the chlorine liberates iodine from the iodide and the starch iodide blue colour is produced. A fleeting blue colour may be due to a local excess concentration of chlorine, so that no note is taken of any colour which does not persist for at least 15 seconds.

This method gives the approximate concentration very rapidly, and has been used in chamber trials, before the trial proper, the concentration being measured accurately later.

COLLECTION OF THE SAMPLE

(see below under "Method" and Fig. 26)

REAGENTS

- (i) Stock 0.1 N arsenite. As in (a) above, but using 5 times the weight of arsenite and bicarbonate.
- (ii) 1% starch solution.
- (iii) Chlorimeter solution. 25 ml of 0.1 N arsenite solution, about 25 ml of starch solution, about 2 g of potassium iodide and 11 g of sodium bicarbonate are dissolved and made up to 1 litre. This solution should be freshly prepared each week.

ANALYTICAL METHOD

The pump should be overhauled if necessary to sample the correct volume of air. The reaction vessel should be well rinsed with the chlorimeter solution, but care should be taken that the inlet tube is kept dry. 10 ml of the chlorimeter solution are now added to the reaction vessel by means of the automatic pipette and the sample of air drawn through by means of the pump, nipping the rubber tubing on each return stroke of the pump to ensure that no solution is blown back into the inlet tube. The chlorine concentration is calculated from the number of pump strokes required before the blue colour persists, e.g. for a 1 in 10,000 concentration in the 100 ml chamber, with a pump aspirating 90 ml of air at each stroke:-

10 litres of chlorine are required

At 20°C 71 g of chlorine occupy 24 litres.

29.6 g are required.

or 0.000296 g Cl_2 per litre of chamber air

10 ml of testing solution contains 0.25 ml 0.1 N arsenite equivalent to 0.0009 g of chlorine

$$\text{Number of pump strokes required} = \frac{0.0009 \times 1,000}{0.000296 \times 90}$$

Hence 1 in 10,000 = 34 pump strokes

or 1 in 1,000 = $3\frac{1}{2}$ pump strokes

Where the number of pump strokes required would be either excessive (very low concentration) or insufficient for the accuracy required the strength of the chlorimeter solution can be varied appropriately.

SECRET

10. CHLOROACETOPHENONE (CN) (1953)

USE

Chloroacetophenone is used in cases when a substitute is required, which will be readily detected by human observers.

PRINCIPLE OF THE METHOD

Use has been made of the general test for methylene ketones known as the Zimmerman Test. It consists briefly of the reaction between the CH_3CO -group and m-dinitrobenzene, which on addition of KOH produces an intense red coloration.

COLLECTION OF SAMPLES

Samples are collected in bubblers containing 20% glycerine in absolute alcohol (vol/vol.). Since the sampling solvent is largely alcohol the method is suitable only for short period samples.

REAGENTS

- (i) m-Dinitro-benzene. The specificity of the reaction is dependent to a large extent upon the purity of the m-dinitro benzene reagent, which must therefore be dealt with as follows:-

20 g pure m-dinitro benzene (m.p. $89-89.5^\circ\text{C}$) is dissolved in 750 ml 95% alcohol, and warmed to 40°C 100 ml 2N NaOH is then added and the mixture cooled after standing for 5 minutes.

(Note: Overheating or prolonged alkali treatment must be avoided).

It is then poured into 2,500 ml water and the precipitate filtered and washed with water on a Buchner filter. After sucking quite free from water, the substance is recrystallised twice, first from 120 ml absolute alcohol, and then from 80 ml.

The resultant dried material should be colourless and of m.p. $90.5^\circ\text{C} - 91^\circ\text{C}$. It should also be tested for purity as follows:-

Equal volumes of 10% alcoholic solution of m-dinitrobenzene and 2N NaOH are mixed. There should be no colouration at the end of 1 hour at room temperature.

Treatment in this manner renders the product free from p-nitro substances and also from thiophene derivatives which give colourations in alkaline solutions with substances other than carboxymethylene groups.

- (ii) Absolute Alcohol. Samples of alcohol containing traces of acetone and aldehydes give blank colours sufficiently high to impair the sensitivity of the method. It has been found necessary to purify the alcohol by distillation first over potash and then over m-phenylene diamine.

- (iii) 6N aqueous KOH.

METHOD

The bubbler contents are made up to a convenient volume with alcohol containing glycerol, a suitable aliquot of not more than 5 ml is taken (if necessary made up to 5 ml with the alcohol/glycerol) and placed in a water bath at 30°C . 0.2 ml of 2% m-dinitrobenzene in absolute alcohol is added. 5 ml of 6N aqueous KOH, also at 30°C is then added and the mixed solution maintained at this temperature for 5 minutes.

SECRET

The colour is measured in the Spekker using the No.5 green filters, and the concentration of chloroacetophenone determined by reference to the calibration curve.

Typical Calibration

mg CN	0.0	0.02	0.04	0.06	0.08	0.10
Spekker reading	0.02	0.10	0.18	0.25	0.32	0.40

SECRET

11. CHLOROPICRIN (ES) (pre 1946)

PRINCIPLE OF THE METHOD

Chloropicrin gives a violet colour with β naphthol and crotonaldehyde in the presence of caustic soda.

COLLECTION OF SAMPLE

Samples are collected in bead bubblers charged with 15 ml absolute alcohol. In order to reduce the losses due to "slip" at 10 l/min., two bubblers should be connected in series.

REAGENTS

- (i) 3 g β -naphthol and 2.5 g crotonaldehyde dissolved and made up to 100 ml with alcohol.
- (ii) 5% aqueous sodium hydroxide
- (iii) Absolute alcohol.

METHOD

The bubbler contents are transferred to a 50 ml graduated flask, the bubbler washed out twice with 10 ml water and then once with 10 ml alcohol, and the sample made to volume with alcohol (i.e. finish with 60% alcohol).

25 ml of this solution or other aliquot are made up to 25 ml with 60% alcohol, 1 ml of the β -naphthol-crotonaldehyde reagent and 2 ml of 5% NaOH are added and mixed. A blank is prepared with 25 ml of 60% alcohol (15 ml alcohol and 10 ml water) and the same quantities of the reagents. The mixture is allowed to stand for 10 minutes and the colour produced by the sample compared directly with that of the blank in the Spekker using the No.5 green filters and the appropriate cell.

Not more than 10 samples can be matched against one blank as the colour begins to fade after 20 minutes.

Notes 1 The estimation should be carried out as soon after sampling as possible to avoid decomposition.

2 Colour development is not reproducible for amounts above 1 mg chloropicrin (a Spekker reading of about 0.50 with the 1 cm cell) so that above this the estimation should be repeated on a smaller aliquot.

CALIBRATION

0.5 g chloropicrin is weighed out in a sealed bulb tube, which is broken in about 100 ml alcohol, and the mixture washed into a 250 ml blackened graduated flask and made up to the mark.

To 5 ml of the solution are added 3.3 ml water and the volume made up to 500 ml with 60% alcohol also in a blackened flask. Suitable aliquots are treated as above.

SECRET

Typical curves

3 cm cells.

mg Chloropicrin	0	0.1	0.2	0.3
Spekker reading	0	0.24	0.48	0.71

1 cm cells.

mg Chloropicrin	0.3	0.5	0.7	0.9	1.0
Spekker reading	0.18	0.29	0.38	0.46	0.5

Note

Possible alternative methods for estimating chloropicrin are:-

1. The resorcinol, potassium cyanide, pyridine method used in the C.W.G.T. Mk.3 - Ptn/4012 (V.6439)
2. Oxidation and production of colour with sulphanilic acid and ethylene diamine - Feinsilver and Oberst, Anal. Chem. 1953, 25, 5.

SECRET

12. CHLOROSULPHONIC ACID

USE

Chlorosulphonic acid is used for smoke production. Estimates have been required of the amount of chlorosulphonic acid (a) falling out of the cloud as gross liquid droplets near the source and (b) in the cloud downwind of the source.

PRINCIPLE OF THE METHOD

The sample is titrated for chloride and for total acidity, and the amount of chlorosulphonic acid calculated, or the sample may be analysed for chloride and for sulphate.

(a) For the gross liquid contamination near the sprayer (pre 1946)

COLLECTION OF SAMPLE

Samples are collected in 32 oz. wide-neck bottles, which can be fitted with ground glass stoppers and which contain a one inch layer of purified dry sand. The sand is purified by first washing with acid to remove soluble salts, then thorough washing with water till all traces of acid have been removed and finally thorough drying.

As soon as possible after the spray, the bottles are stoppered.

METHOD

100 ml of water are added quickly and the stopper immediately replaced. The mixture is allowed to stand for about one hour (till all fumes have disappeared) with occasional shaking.

If the amount in the sample is small, so that the volume of acid as compared with 100 ml can be neglected, an aliquot can be taken directly from the bottle. For heavy samples, the contents are filtered washed and made up to a standard volume e.g. 250 ml, and a suitable aliquot taken.

Titration is carried out with 0.1 N sodium hydroxide using 2.5 dinitrophenol as indicator (phenolphthalein can be used if the alkali is carbonate free); this gives total acidity. N nitric acid is then added till the acidity is 0.04 N and the chloride is titrated with 0.1 N mercuric nitrate using diphenyl carbazone as indicator.

The HClSO_3 present is calculated from the chloride titration.

The free SO_3 present is calculated from the difference between the total acid titre and the calculated HClSO_3 .

i.e. Titre for $\text{SO}_3 = \text{total acid titre} - 3 \times \text{Cl}^- \text{ titre}$

(b) For estimation of the smoke

COLLECTION OF SAMPLE

The smoke is absorbed on a filter (a double cone filter containing filter paper) backed by a bubbler charged with distilled water.

SECRET

METHOD

The filter paper is placed in a conical beaker to which the bubbler contents and washings are added, and a few minutes are allowed for the acid to extract.

Either two separate aliquots are taken and one is titrated for total acidity to B.D.H. 4.5 indicator and the other for chloride, or the whole extract is titrated with standard NaOH using 2,5 dinitrophenol as indicator, and the acidity then adjusted with acetic acid and the mixture titrated potentiometrically for chloride (q.v.).

SECRET

13. CYANIDE

USE

A non-specific method which has been used for the analysis of hydrogen cyanide and of GA.

PRINCIPLE OF THE METHOD

The cyanide ion (produced by hydrolysis if necessary) is converted to CNBr, the excess bromine is destroyed, and the CNBr reacted with pyridine and benzidine to give a colour.

COLLECTION OF THE SAMPLE

The sample is collected in bubblers charged with N.NaOH.

REAGENTS

- (i) N.NaOH.
- (ii) 2N Acetic acid (120 ml glacial acetic acid made up to 1 litre with distilled water).
- (iii) 50% Glacial acetic acid.
- (iv) Saturated solution of bromine in water.
- (v) Pyridine reagent - 25 ml of freshly redistilled pyridine and 2 ml conc. HCl made up to 50 ml with distilled water.
- (vi) 1.5% Sodium arsenite in water.
- (vii) 3% Benzidine in pure alcohol.

ANALYTICAL METHOD

An aliquot of not more than 5 ml, containing between 0.002 and 0.02 mg CN⁻ is placed in a tube graduated at 10 ml. The aliquot is neutralised and made slightly acid by the addition of a calculated quantity of acetic acid, either 2N or 8N (50% glacial) strength as convenient so that the total volume does not exceed 5.9 ml (Note: the sample should be made acid only immediately before analysis or some HCN may be lost).

0.3 ml bromine water is added and mixed, and the mixture allowed to stand for 2 minutes.. 0.50 ml of 1.5% sodium arsenite solution is added and mixed, and the mixture allowed to stand for a further 2 mins. 0.80 ml of benzidine solution and 2.5 ml of pyridine reagent are added and the solution made up to the 10 ml mark with distilled water, mixed well, and allowed to stand for a further 10 mins. The colour is then measured in the "Spekker" using the No.6 light blue screens.

Notes:

- (1) The amount of sodium arsenite added must be sufficient to discharge all the colour of the free bromine.
- (2) Strict adherence to the time schedule is essential.
- (3) The solutions must be mixed thoroughly, either by using a glass mixing rod which is left in the solution for the whole period, or by flicking the tube. The thumb or finger must not be allowed to come in contact with the solution.
- (4) With two operators, batches of 12 samples can be processed with 1 minute intervals between samples and a 15 minute interval between batches.

CALIBRATION

The calibration is carried out on a standard solution of potassium cyanide.

SECRET

11. CYANOGEN CHLORIDE

(a) Macro Method (1951)

PRINCIPLE

Cyanogen chloride is hydrolysed by alcoholic soda and the cyanide and chloride titrated together by Volhard's method in acid solution.

COLLECTION OF THE SAMPLE

Samples are collected at suitable flow rates (from 1 to 40 litres/min.) in sintered glass bubblers containing 100 ml 4% alcoholic sodium hydroxide.

REAGENTS

- (i) 0.1 N. AgNO_3
- (ii) 0.1 N. KONS
- (iii) Ferric alum solution

ANALYTICAL METHOD

The bubbler contents are washed out into a conical flask with distilled water, acidified with nitric acid and a few drops of ferric alum solution added.

20 ml of 0.1 N silver nitrate solution is added, and, after shaking to coagulate the precipitate, the excess is back titrated with 0.1 N potassium thiocyanate

$$1 \text{ ml } 0.1 \text{ N. } \text{AgNO}_3 = 6.15 \text{ mg } \text{CNCl}$$

SECRET

14. CYANOGEN CHLORIDE cont'd.

(b) Micro Method (1951)

PRINCIPLE

Cyanogen chloride reacts with pyridine in the presence of a small amount of benzidine hydrochloride to give an intense reddish colour.

COLLECTION OF THE SAMPLE

Samples are collected in miniature bubblers containing 2.5 ml of a solution of 0.1 g benzidine hydrochloride in 100 ml of pure fractionated pyridine. Any evaporated pyridine is replaced after sampling. The samples must not be allowed to stand for more than 1 hour before analysis.

REAGENTS

- (i) Benzidine pyridine reagent - 0.1 g benzidine in 100 ml pure fractionated pyridine.
- (ii) Conc. HCl.

ANALYTICAL METHOD

The sample is made up to 10 ml with benzidine pyridine reagent, and to the whole (or a suitable aliquot made up to 10 ml with the reagent) is added 0.5 ml conc. hydrochloric acid, and the tube placed in a boiling water bath for 1.5 to 2 minutes.

After cooling, 5 ml of distilled water are added and the colour measured immediately in the "Spekker" using the No.5 green screens, or in the "Unican" at a wave-length of 515 mμ.

CALIBRATION

A solution of cyanogen chloride in absolute alcohol is standardised by the Volhard method (above), diluted, and aliquots treated as above.

Note:

Solutions of cyanogen chloride (e.g. in cyclohexanol) can be analysed by the indole perborate method as used for G gases, but a suitable sampling technique for this method has not yet been found. (The slip of cyanogen chloride through cyclohexanol in a miniature bubbler is excessive.)

SECRET

15. DICHLORO DIETHYL ETHER(1946)

USE

Dichloro diethyl ether is used as an innocuous substitute when methyl salicylate is unsuitable or unobtainable.

PRINCIPLE

On heating dichloro diethyl ether with pyridine to 95°C, a yellow colour is produced.

COLLECTION OF THE SAMPLE

Samples are collected in bubblers charged with 15 ml pure pyridine, and fitted with small soda-line guard tubes. Sampling duration may be up to 30 mins. under temperate conditions.

REAGENTS

- (i) Pure, redistilled pyridine, fraction 113° - 114°.
- (ii) 95% solution by volume of above, in water.
- (iii) 0.2 N sodium hydroxide solution.
- (iv) 2% Gum ghatti solution, prepared by suspending 2 g gum in a muslin bag in 100 ml water overnight, and filtering before use.

ANALYTICAL METHOD

The bubbler contents are washed into clean, dry 25 ml cylinders with pure pyridine, up to a volume of 19 ml. 1 ml water is then added from a pipette to give a final concentration of 95% pyridine. The solution is well mixed, and a suitable aliquot portion, (not more than 1/2) is placed in a clean dry tube, and diluted to 10 ml with 95% pyridine.

The tube is then placed in a water bath maintained at 95°C for 120 min. It is then cooled, 0.5 ml gum ghatti solution added, the tube shaken, and 0.5 ml 0.2 N NaOH solution added, followed by immediate shaking.

The yellow colour is read off after 10 mins. in the Spekker Absorptiometer, using No.7 dark blue screens.

CALIBRATION CURVE

This is prepared by weighing pure DDE into a flask, and diluting with 95% pyridine. Suitable amounts of this solution are then used for preparing a calibration curve by the method given above.

A typical calibration curve done in duplicate gave the following readings

mg DDE	0	.02	.04	.06	.08
Spekker reading	0,0	.08, .08	.14, .17	.24, .245	.285, .27

mg DDE	0.1	0.2	0.4	0.6	0.8	1.0
Spekker reading	.305, .32	.46, .47	.57, .59	.68, .70	.76, .76	.80, .81

Above 0.4 mg DDE, the curve becomes rather flat, and the accuracy is not very great.

SECRET

16. DYE (1954)

USE

Dyes are used as characterisers. They give a rapid visual assessment of the position and degree of any liquid contamination.

They show the amount of contamination which would have occurred if there had been no losses by evaporation, hydrolysis, etc. (unless the loss due to evaporation is so great that the droplet has completely vapourised and the dry dye blows away) and by comparison of dye content and agent content of the droplets a measure of these losses can often be obtained.

SELECTION OF THE DYE-STUFF

The particular dye used is selected for:-

- (a) Solubility and stability in the agent
- (b) Colour in contrast with natural colours (Reds are therefore usually preferred as giving the greatest contrast with green grass.)
- (c) Stability to light and on storage on the sampling material - paper envelope, woollen felt, or turf.
- (d) Lack of solubility in water (rain or dew effects).
- (e) Ease of extraction from the sampling material.
- (f) Intensity of colour.

In the past, Oil Yellow and Waxoline Red have been used extensively. Oil Yellow is appreciably soluble in many agents, including mustard gas, but it has a very poor colour until acidified and it proved unsuitable for measuring stain sizes. It is also somewhat volatile and therefore has poor storage properties. Waxoline Red is not very soluble in most agents.

At present (1955) the following dyestuffs are favoured:-

For GB: Violet Dye, Clayton TT3809 (This is the unsulphonated base of Fast Acid Violet A2R, Colour Index No. 758).

This dye is at least 20% soluble in GB and can be extracted from paper and woollen felt pads by methyl cellosolve. It gives spots with a sharply defined edge (on paper) and is therefore very suitable for measuring drop size.

It is not very fast to light (although it can be exposed to winter sunlight for 15 hours without loss) and therefore papers should be removed to the dark as soon as possible after a trial. This is not so important with felt pads as the thickness of the pad gives some protection.

This dye is not easily extracted from turf.

For MA: Orasol Red B

This is one of the few dyes which are very soluble in methyl acetoacetate. The methyl acetoacetate should be kept in a glass container as long as possible and charged into metal only just before the trial to avoid the production of a colour from the reaction of the MA on the iron, which could be confused with the orange or red dye.

Orasol Red B is readily extracted by industrial spirit.

SECRET

For MS: Waxoline Red

The pads, papers or turves are extracted with cold chloroform.

COLLECTION OF THE SAMPLE

The sample is collected on sampling envelopes, felt pads, turf, etc. (see Section II, 3 above) or on cascade impactor slides.

REAGENTS AND METHOD OF ANALYSIS

(a) Violet Dye Clayton TT3809

Reagents (i) Methyl cellosolve

(ii) Acid cellosolve "A" 90 ml methyl cellosolve
10 ml conc. sulphuric acid

(iii) Acid cellosolve "B" 90 ml methyl cellosolve
10 ml Acid cellosolve "A"

Recovery of cellosolve The used cellosolve is allowed to stand over quicklime, filtered and then distilled over copper powder with a little ferrous sulphate. Care should be taken to prevent the distillation going too far, as cellosolve is liable to peroxidise and explode. The portion distilling between 116°C and 120°C is suitable for re-use.

Paper or felt pad Each unit is soaked in 225 ml of cold methyl cellosolve until the dye is extracted. This requires at least 1 hour, with frequent shaking; heavily contaminated pads may require soaking overnight. The extract is filtered and to 45 ml of the filtrate are added 5 ml of acid cellosolve "A". Either this solution, or a suitable aliquot diluted with acid cellosolve "B", is used to measure the colour on the Unicam SP.350 Spectrophotometer at a wave length of 535 millimicrons.

Turf: The turf is soaked in 450 ml of cold methyl cellosolve for 48 hours, with occasional shaking the turf being broken up as far as possible. The extract is filtered, and to 45 ml of the filtrate are added 5 ml of acid cellosolve "A". The mixture is re-aliquoted and diluted with acid cellosolve "B". The colour is then measured on the Unicam at both 535 mμ and 430 mμ and the amount of dye estimated by means of a nomogram.

(b) Orasol Red B

The dye is extracted with industrial spirit, using 200 ml for pads or envelopes and 500 ml for turves, and the colour measured on the Unicam at a wave length of 520 mμ.

(c) Waxoline Red

The dye is extracted with chloroform, using 250 ml for at least 1 hour for pads and envelopes (if papers are damp they may require soaking overnight), and 500 ml for turves with at least 2 hours soaking.

The colour is measured on the Unicam at a wave length of 525 mμ for pads and envelopes, and for turves at 525 mμ and 654 mμ using a nomogram.

SECRET

Preparation of Calibration curve

The calibration curve should be prepared from the actual charging used in the weapon and not from a sample of pure dye, as this will allow for any interference from the agent itself, from reaction with the case of the weapon and for any inaccuracy in the preparation. When curves are included in the samples, the nomogram should be prepared with charging which has been diluted with an extract from a blank turf similar to those cut for the samples and not with pure solvent. For very heavily contaminated turves, the sample extract may require dilution with fresh solvent to such an extent that the interference of the green colour is negligible and in this case the nomogram will not be required.

PREPARATION OF A NOMOGRAM FOR THE COLORIMETRIC ESTIMATION OF ONE DYE STUFF IN THE PRESENCE OF ANOTHER

In order to estimate the concentration of red dyestuff in presence of a green one, measurements of the optical density are made at two wavelengths. It is known that the scale reading of the instrument used is proportional to concentration, for solutions of the red dye alone. It is believed that this is true also for the green dye, and that the two do not interact in solution. In these circumstances the density reading will be the sum of contributions from the two dyes separately.

At wavelength λ_1 , then

$$X_1 = \alpha(\rho_1 r + \gamma_1 g)$$

and at λ_2

$$X_2 = \alpha(\rho_2 r + \gamma_2 g)$$

where X_1, X_2 are the scale readings at λ_1, λ_2 respectively, ρ_1 and ρ_2 are the specific absorptions of the red dye, γ_1 and γ_2 the specific absorptions of the green, r and g the amounts of the red and green dyes respectively, and α is a constant depending on the instrument and depth of liquid measured.

Eliminating the unknown, g , which is in any case not required, gives

$$r = \frac{1}{\alpha \rho_1 - \rho_2 \gamma_1 / \gamma_2} \left(X_1 - X_2 \frac{\gamma_1}{\gamma_2} \right)$$

The constants in this equation can be measured, but it is probably better to treat it empirically. It may be written

$$r = AX_1 - BX_2;$$

then if measurements at λ_1 and λ_2 are made on a few mixtures containing known amounts of red dye, good average values of A and B can be obtained by the method of least squares. This will to some extent take account of small deviations from Beer's law, etc.

SECRET

For instance, if two pairs of solutions are made, one pair containing a known concentration say r_a of red dye but differing (unknown) concentrations of green, the other containing a known concentration, say r_b of red dye but again, differing concentration of green, and all four solutions are measured at the two wavelengths A and B can be calculated from:

$$A = \frac{(\Sigma r X_1)(\Sigma X_2^2) - (\Sigma r X_2)(\Sigma X_1 X_2)}{(\Sigma X_1^2)(\Sigma X_2^2) - (\Sigma X_1 X_2)^2}$$

$$B = \frac{(\Sigma r X_1)(\Sigma X_1 X_2) - (\Sigma r X_2)(\Sigma X_1^2)}{(\Sigma X_1^2)(\Sigma X_2^2) - (\Sigma X_1 X_2)^2}$$

A nomogram is constructed as follows:

3 parallel vertical lines are drawn. These will be, reading from the left say, the X_1 , r and X_2 scales. The distance between the X_1 and r scales must be B units (e.g. if $B = 2$, 1 inch = 2×0.5 inch would be convenient) and that between the r and X_2 scales, A of the same units (e.g. if $A = 10$, 5 inches = 10×0.5 inches). Two parallel lines are drawn cutting the first 3 at right angles, at a distance apart equal to the desired length of the X scales (e.g. 5 inches).

The intersections are marked as follows:

Upper line and X_1 scale	- - -	$X_1 = 1.0$
" " " X_2 "	- - -	$X_2 = 0.0$
Lower line and X_1 "	- - -	$X_1 = 0.0$
" " " X_2 "	- - -	$X_2 = 1.0$

The X scales are subdivided linearly.

Now X_1 is calculated when $X_2 = 1$ and $r = 0$. $X_1 = B/A$

This point is marked on the X_1 scale and joined to $X_2 = 1$. The intersection with the r scale is $r = 0$. Then X_1 is calculated when $X_2 = 0$ and $r = 10$:

$X_1 = 10/A$. This point is marked and joined to $X_2 = 0$. The intersection is $r = 10$ on the r scale. The two points $r = 10$ and $r = 0$ are now known; their distance apart can be measured and the r scale subdivided.

The starting points here have been chosen to cover the range known to be needed.

SECRET

17. ETHYL CHLORO ACETATE (1948)

USE

Ethyl chloroacetate has been used as a substitute for GB, being very similar in some of its physical properties.

PRINCIPLE

The ethyl chloroacetate is hydrolysed and the chloride estimated.

COLLECTION OF THE SAMPLE

Vapour samples are collected at 10 l/min. in bubblers charged with a 5% solution of sodium hydroxide in water containing 10% of absolute alcohol. This gives a lower and more uniform "slip" than using aqueous sodium hydroxide.

REAGENTS

- (i) 0.002 N silver nitrate solution, freshly prepared each day by dilution from 0.02 N solution.
- (ii) Conductivity water.
- (iii) Aqueous acetic acid (50% by vol.)

METHOD

The bubbler contents are washed out into a round bottomed flask, boiled under a reflux condenser for 30 mins., cooled and the chloride titrated electrometrically after acidification with 2 ml of 50% acetic acid.

$$1 \text{ ml } 0.002 \text{ N AgNO}_3 \equiv 0.245 \text{ mg ECA}$$

A blank determination is made for each batch of samples. This blank varies according to the aliquot taken and is largely due to the impurities in the sodium hydroxide.

Note:

Care should be taken to avoid contamination by adventitious chlorides, e.g. on Porton ranges positive results were obtained with shells charged distilled water fired into the ground upwind of the bubblers.

SECRET

18. FERRIC CHLORIDE (1952)

USE

Ferric chloride has been used as a non-toxic smoke.

PRINCIPLE

Ferric chloride gives a blue colour with thioglycollic acid in ammoniacal solution.

COLLECTION OF THE SAMPLE

The smoke is sampled on one Whatman No. 44 paper in a double cone filter by aspiration at either 1 l/min. or 10 l/minute.

REAGENTS

- (i) Thioglycollic acid (90%)
- (ii) Dilute hydrochloric acid (HCl/Water 1/27)
- (iii) Dilute ammonia (NH_4OH (0.880)/Water 1.1)

ANALYTICAL METHOD

The paper is extracted with 20 ml dilute hydrochloric acid with occasional shaking for 3 hours or more, and the extract filtered. 15 ml of the filtrate are pipetted into a 1" boiling tube and 5 drops of thioglycollic acid added. The mixture is shaken, and 5 ml 1/1 ammonia added and again shaken well. After allowing to stand for 10 mins., the colour is measured on the Spekker using the yellow green screens (605) and the appropriate cell.

Blank tests should be carried out on unused filter papers.

TYPICAL CALIBRATION CURVE

Obtained by using a solution of "Analar" ferric alum:

$\mu\text{g Fe}^{+++}$	11.1	22.2	33.3	44.4	55.6	66.8	89.0
Spekker reading	0.12	0.23	0.33	0.44	0.55	0.66	0.90

Note:

1: 10 phenanthroline, which is expected to be a more sensitive reagent for Fe^{+++} , has not yet been tested.

SECRET

19. FLUORIDE

(a) By amperometric titration with thorium nitrate (1953)

PRINCIPLE

A solution containing fluoride ion is titrated with thorium nitrate in a glass tube containing a dropping mercury electrode and a mercury pool with a potential of -1.46 volts applied (a little more negative than the half wave of thorium nitrate). The current remains almost constant until all the fluoride ion has been removed from solution, after which it increases sharply in direct proportion to the excess of thorium nitrate in solution.

G compounds are first hydrolysed to give the fluoride ion, the solution neutralised and the phosphorus compounds which would interfere with the titration precipitated by the addition of an excess of silver nitrate, the latter being precipitated in turn with potassium chloride.

REAGENTS

- (i) N KOH (for hydrolysis)
- (ii) Dilute HNO_3 (pH 6.5)
- (iii) 0.1 N AgNO_3
- (iv) 0.1 N KCl
- (v) 0.1 N KNO_3
- (vi) 0.05 M $\text{Th}(\text{NO}_3)_4$ in 0.1 N KNO_3
- (vii) 0.01 M $\text{Th}(\text{NO}_3)_4$ in 0.1 N KNO_3

APPARATUS

This is illustrated in Fig. 27, and details are given in P.T.P. 342.

METHOD (for GB)

0.2 to 0.3 gram of GB is weighed into a small flask, 10 ml of N KOH solution is added and the mixture allowed to stand for at least 10 minutes. One drop of Universal Indicator is then added and the solution neutralised with dilute nitric acid (pH 6.5), and made up to 100 ml or other suitable volume.

1 ml of the hydrolysed G solution, estimated to contain between 10 and 800 μg of fluoride ion, is measured from a microburette into the titration cell (a 3" by $\frac{1}{2}$ " specimen tube) followed by 1 ml 0.1 N AgNO_3 , 1 ml 0.1 N KCl, and 1 ml 0.1 N KNO_3 . Clean mercury is added to the titration cell to a depth of about $\frac{1}{4}$ ", and the cell is placed in the burette stand. The dropping mercury electrode, the contact wire to the mercury pool, the air stirrer tube and the burette are placed in position. The instrument is set to apply 1.46 volts across the cell, the "backing out" resistance is adjusted, if necessary, to bring the galvanometer to a low reading, and the sensitivity control adjusted so that the whole of the titration readings may be made on the galvanometer scale.

SECRET

Additions of 0.05 ml. of standard thorium nitrate solution are made, (using 0.01 M for quantities up to 100 μ g of fluoride ion and 0.05 M for quantities expected to be greater than this). After each addition, the solution is stirred by blowing a little air through the stirrer tube from a blow-bulb and the galvanometer reading taken as soon as it has become steady. The readings are plotted against volume of titrant and the intersection of the two straight lines produced gives the endpoint.

Note:

A method using a "High Frequency Titrimeter" has also been used for the estimation of fluoride ion in GB, where about 0.3 g of the sample was available. Details are given in P.T.P.231.

SECRET

Fluoride (cont'd.)

(b) By Thorium Nitrate and Solochrome Blue (1946)

PRINCIPLE

When a sample of a fluoride is buffered to pH 3.0 and titrated with thorium nitrate in the presence of solochrome blue, a blue lake is formed at the end-point and is matched against a blank containing a trace of thorium nitrate.

COLLECTION

GB vapour is collected in bubblers containing N sodium hydroxide.

REAGENTS

- (i) Dilute perchloric acid ($\frac{N}{10}$ or $\frac{N}{50}$)
- (ii) Standard thorium nitrate 0.004 N (552 mg $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in 1 litre of water.)
- (iii) Solochrome Brilliant Blue BS 0.02% solution in water
- (iv) Chloroacetic buffer - 22.7 g monochloroacetic acid in 100 ml of water. 50 ml of this solution are neutralised with 6N NaOH, and this is then added to the remaining (unneutralised) 50 ml and the combined portion made up to 1 litre.

METHOD

A suitable aliquot containing less than 100 μg of F⁻ is taken for titration. This is placed in a Nessler glass (standing on a white tile), and made up to 50 ml with distilled water. Phenolphthalein is added, followed by perchloric acid until the pink colour is just destroyed. 1 ml of dye solution is added and then more perchloric acid solution until the yellow colour of the dye just changes to pink. 0.5 ml chloroacetic acid buffer is then added.

To a similar Nessler tube is added an amount of caustic soda solution equivalent to that in the sample tube, and this is treated in a similar manner. 0.1 ml of 0.004 N thorium nitrate is then added, changing the colour from pink to bluish purple.

The sample is then titrated with the 0.004 N thorium nitrate from a micro burette until it exactly matches the colour of the blank. 0.1 ml (the volume of thorium nitrate added to the control solution) is deducted from the burette reading and the net reading referred to the calibration curve.

Owing to personal variation in judging the end point, the calibration curve should be prepared by the same operator at the same time as the analysis of the samples.

Typical calibration curve:

μg Fluorine	5	10	20	40	60
ml 0.004 thorium nitrate	0.25	0.40	0.72	1.39	2.00

For modifications of this method for

PF3 - see PR 2549

Methyl fluoroacetate - see PR 2556

SECRET

20. FURFURAL (1954)

USE

Furfural, containing 10% of carbon tetrachloride to reduce the risk of inflaming, has been used as a substitute where it was desired to show visually by the change in colour of the solution in the bubblers the extent and the magnitude of the concentrations produced.

PRINCIPLE OF THE METHOD

Furfural gives a deep red colour with aniline acetate.

COLLECTION OF THE SAMPLE

Miniature bubblers charged with 5 ml of a 10% solution of aniline in 50/50 glacial acetic acid/water and operated at 1 litre/min. are used to sample furfural.

ANALYTICAL METHOD

The depth of colour is proportional to the amount of furfural, but the colour begins to fade after about 5 mins. and is appreciable after 1 hour.

This rough visual estimation has been sufficient for all requirements up to date, but the method could probably be made quantitative by sampling in acetic acid and then adding the aniline in the laboratory and measuring the colour at a fixed time after this addition.

SECRET

21. G AGENTS

(a) By cyanide (GA) (1948)

The sample is collected in bubblers charged with N NaOH. An aliquot to contain between 0.01 and 0.12 mg GA is taken and analysed as for cyanide (see 13 above).

SECRET

G agents (cont'd.)

(b) By phosphate (1951)

This method estimates the total G agent including any decomposition products, so that if used in conjunction with the dianisidine method (see below) a measure of the amount of hydrolysis can be obtained.

COLLECTION OF THE SAMPLE

The vapour is collected in bubblers charged with N NaOH.

REAGENTS

- (i) N NaOH
- (ii) 5 N H₂SO₄
- (iii) 10% ammonium persulphate. 10 g (NH₄)₂ S₂O₈ to 100 ml with water.
- (iv) 8.5% sodium molybdate solution.
- (v) 40% stannous chloride. 40 g SnCl₂ dissolved in 86 ml conc. HCl and made up to 100 ml with more conc. HCl if necessary. This solution should be kept in the dark and not be stored for more than a month.
- (vi) 0.2% stannous chloride. 1 ml of the strong solution diluted to 200 ml with distilled water. This solution should be freshly made when required and not kept for more than an hour or two.

METHOD

A suitable aliquot is used as follows:-

5 ml aliquot to contain	0.01 to 0.08 mg
2 ml " "	0.01 to 0.08 mg
1 ml " "	(0.01 to 2.0 mg GD
	(0.01 to 5.0 mg GB or GE

For 5 ml or 2 ml aliquots

The volume is made up to 5 ml with N NaOH, in a 1" boiling tube, 2.7 ml of 5 N H₂SO₄ (to neutralise and give 2 ml excess) and 1 ml of 10% ammonium persulphate are added and the tube placed in a boiling water bath for 30 mins. The tube is washed out into a tube graduated at 8 ml and the volume made up to 8 ml. 1 ml sodium molybdate solution and 1 ml dilute stannous chloride solution are added and the mixture shaken (Note: The temperature should be between 15°C and 40°C. The molybdate and stannous chloride solutions should be blown from pipettes into the main solution to give good and immediate mixing.) The colour produced after 5 mins. is measured on the Spekker using the red screens.

For 1 ml aliquots

The aliquot is placed in a 5/8" tube graduated at 8 ml., 1 ml ammonium persulphate is added and the tube placed in a boiling water bath for 30 mins. If necessary the mixture is diluted and re-aliquoted. 2 ml of 5 N H₂SO₄ are added to the mixture, diluted to 8 ml and the above procedure carried out.

SECRET

Typical Calibration Curve

The calibration curve is prepared using potassium dihydrogen phosphate A.R., 1 to 5 ml of an aqueous solution being boiled, cooled, acidified with 2 ml 5 N H_2SO_4 , diluted to 8 ml and treated as above. This curve can then be used to check the purity (by phosphorus content) of the liquid G agent.

µg P	0	2.0	4.0	6.0	8.0	10.0	15.0	20.0
Spekker Reading	.08	.19	.305	.42	.54	.65	.91	1.14

Note: A similar blue colour is given by arsenic and silicon which may be obtained in traces from some types of glass. All boiling tubes, test tubes and should therefore be treated with sulphuric acid, ammonium persulphate etc. until they give a reasonable blank reading.

Modification when the sample is taken in isopropanol (1952)

For some purposes, e.g. the collection of liquid drops, it is impracticable to take separate samples for analysis by the phosphorus and dianisidine methods. In these cases the sample is collected in isopropanol and the G content determined by the two different methods on aliquots from the same solution. Thus, with dyed GB droplets, estimation of the dye, GB by phosphorus and GB by dianisidine has been used to determine the degree of evaporation and of hydrolysis.

To an aliquot of not more than 2 ml of the isopropanol solution, 1 ml of 10% ammonia (1 vol. NH_4OH .880 plus 2 vols water) is added, the mixture shaken well and allowed to stand for at least 1 hour. It is then placed in a boiling water bath for 1 hour to evaporate the isopropanol and if necessary topped up with water to maintain the volume at, about, but not above 1 ml. 1 ml 10% ammonium persulphate is added and the mixture is replaced in the boiling water bath for 30 mins. If necessary it is diluted and realiquoted. If the whole sample has been taken, 1.8 ml 5 N H_2SO_4 are added; if half has been used, 1.9 ml 5 N H_2SO_4 are added (to give a total of 2 ml of acid including that from the persulphate). After dilution to 8 ml, the estimation is continued as above.

SECRET

G agents (cont'd.)

(c) Macro method for phosphorus in G compounds (1951)

This method is suitable for quantities of G agent of the order of 0.2 g.

REAGENTS

- (i) Sodium Hydroxide AR.
- (ii) Fusion mixture - equal parts Na_2CO_3 and K_2CO_3
- (iii) Nitric acid SG 1.2 900 ml conc. HNO_3 and
1200 ml water
- (iv) Ammonium nitro molybdate - 30 g ammonium molybdate dissolved
in 200 ml water and added gradually with constant stirring to
200 ml nitric acid.
- (v) Magnesium mixture - 55 g magnesium chloride and 100 g ammonium
chloride dissolved in water and diluted to 1 litre.
- (vi) Ammoniacal ammonium chloride solution 50 g NH_4Cl dissolved in
water: 100 ml 0.88 ammonia added and diluted to 1 litre with
water.
- (vii) 2% Nitric acid solution
- (viii) 3% Ammonia solution
- (ix) 10% Ammonia solution
- (x) Ammonium nitrate.

METHOD

About 2 g sodium hydroxide are dissolved in as little water as possible in a platinum crucible. A definite amount of G agent (about 0.2 g) is weighed into this crucible and allowed to stand to hydrolyse. About 3 g fusion mixture is added and heated very gently at first, till all the water has evaporated, and then more strongly till the mixture has fused and decomposed the G agent. After cooling, the contents of the crucible are dissolved in water and washed into a beaker. 50 ml nitric acid (SG 1.2) and about 7 g ammonium nitrate are added and the mixture heated to 75 - 80°C. 50 ml ammonium nitro molybdate are heated to 75 - 80°C, and the two solutions are mixed and allowed to stand overnight. The temperature at the time of precipitation must not exceed 80°C or some molybdic acid will be produced.

The ammonium phosphomolybdate is filtered off and the precipitate washed several times with 2% nitric acid solution. It is then dissolved in as little 10% ammonia solution as possible, washing the filter paper with 3% ammonia solution, and re-filtered if necessary. To the clear solution 50 ml of magnesia mixture are added gradually with constant shaking, and the precipitate allowed to stand overnight.

The mixture is filtered through a No.42 or 44 Whatman paper, and the precipitate washed well with the ammoniacal ammonium chloride solution. The paper is transferred to a weighed platinum crucible and ignited gently at first, then more strongly and finally reweighed.

Conversion factor: $\text{Mg}_2\text{P}_2\text{O}_7 \times 0.2787 = 2\text{P}$

SECRET

G agents (cont'd.)

(d) By dianisidine (1955)

This method is comparatively specific for organic phosphorus-fluorine compounds and is used to determine undecomposed G gas.

PRINCIPLE

In the presence of hydrogen peroxide, G gases react with amines of the dianisidine type to give a brown colour. The method is very sensitive to pH; in strongly alkaline solutions the colour is developed quickly and fades quickly; in slightly alkaline solutions it develops very slowly. A pH of 11.7 has been found to be the most satisfactory for stability of colour. The method is also affected by changes in the temperature of the reagents and by impurities which are normally present in bulk supplies of acetone, so that the acetone used has to be purified carefully.

COLLECTION OF THE SAMPLE

The vapour is collected at 1 l/min. in miniature bubblers which are graduated at 25 ml and are charged with cyclohexanol containing 5% methyl cellosolve (ethylene glycol mono methyl ether). 2 ml of solvent is sufficient for sampling up to 10 mins. at temperatures from 35°F to 90°F but for longer periods or more extreme temperatures 5 ml should be used, as can be noted from the following "Slip" values

Sampling of GB in miniature bubblers charged with cyclohexanol containing 5% methyl cellosolve % slip

With 2 ml solvent:

Temperature:	Time of Sampling (Mins.)			
	1	5	15	30
40°F :	4	9	14	15
50° :	4	8	12	14
63° :		6	10	14
77° :	4	7		23
97° :	4	9	17	34

With 5 ml solvent:

40° :	3	4	8
50° :	2	4	7
77° :	2	3	9
97° :	2	3	11

Note Sampling of GB at high flow rates:-

In cases where it is desired to sample the GB concentration at a high flow rate (e.g. to simulate human breathing rates, or to avoid taking a fraction from a high-rate flow line) either large sintered glass bubblers or solid absorbent tubes may be used.

Large bubblers are charged with cyclohexanol solvent as usual, an aliquot of not more than 5 ml taken and the analysis carried out in the usual way.

Solid absorbent tubes are charged with impregnated silica gel, prepared as follows:-

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The gel is sieved (sieve - 18 mesh per inch) and all fines rejected in order not to introduce a high resistance to the air flow. 10 g of this gel is placed in 500 ml of 1% potassium dihydrogen phosphate solution and the solution gently heated to 50°C with stirring to expel air bubbles. The gel is then filtered through a Buchner funnel and air-dried on the funnel for 5 mins., then dried in an oven at 150°C for 2 hours.

Using 3 g of impregnated gel in the solid absorbent tube samples may be taken at flow rates up to 20 litres/min.

As GB is unstable on moist silica gel, the tubes should be stored in a sealed container or in a desiccator until required and the samples must be extracted immediately after sampling. The silica gel is emptied from the tube into a flask containing 15 ml of acetone buffer pH 5.5 (2.72 g KH_2PO_4 in 1 litre of water and 1 litre of acetone added and mixed). After extraction the solution is filtered and a suitable aliquot of not more than 5 ml is then analysed by the usual method (see below)

REAGENT

- (i) Stock Buffer 40 g A.R. KH_2PO_4 to 1 litre in
22.5 g A.R. KOH) distilled water
- (ii) Buffer for use. Mix 1 vol. of stock buffer, $1\frac{1}{2}$ vols. of distilled water and 2.5 vols. of purified acetone.

This diluted buffer should be kept away from strong sunlight and should not be stored for more than 7 days. Storage temperature not less than 15°C.

- (iii) Hydrogen peroxide - 1% H_2O_2
- (iv) Diamisidine Hydrochloride - 1.3 g to 100 ml in distilled water. This solution should be stored in the dark and for not more than 7 days.

* Tests for purity of acetone - see below

PROCEDURE

Immediately before each batch of samples is analysed, 23 vols. i, 1 vol. ii, and 1 vol. iii are mixed, 20 samples forms a convenient batch, so that normally, 460 ml i, 20 ml ii and 20 ml iii are used. The inlet tube is removed from the bubbler and the latter filled to the 25 ml mark with this mixed reagent. The inlet tube is replaced 3 or 4 times, allowing to drain in between, in order to wash out the cyclohexanol from the capillary. The inlet tube is again removed and the bubbler contents thoroughly mixed, using a glass rod with the end flattened to a diameter a little less than that of the tube. The process is repeated with the other samples of the batch at 1 minute intervals. This procedure should be carried out first on a "blank" 2 ml of cyclohexanol which is then used to fill the Spekker reference cells. The colour intensity of the samples is measured exactly 10 mins. after adding the reagent to the bubbler, using either the 3 cm, 1 cm., 0.5 cm. or 0.25 cm. cell as appropriate and Spectrum Violet 601 screens.

SECRET

On cold days, care should be taken that the temperature of the reagents does not fall below 15°C , and under hot conditions the reagents should be kept in a cooling bath to keep them below 25°C .

Notes

(1) The following solutions have been found useful for checking that the efficiency of the Spekker is unchanged:

A. 0.7 g A.R. $\text{K}_2\text{Cr}_2\text{O}_7$ per litre

B. 0.35 g

C. 0.175 g

(2) The Spekker lamp should be switched on 10 mins. before use in order to become stabilised.

(3) Batches of samples should not normally exceed 20 as the "blank" develops a colour slowly and it is advisable to empty and refill the reference cells not more than 30 mins. after the reagent was first mixed.

(4) The method is interfered with by traces of methyl acetoacetate and also by impurities commonly present in acetone.

Purification of Acetone

100 g KMnO_4 is added to each 5 gals and allowed to stand with occasional shaking for at least 10 days. The mixture is then distilled through a reflux head.

Tests for purity of acetone

(1) Agulhon's Test

Reagent - 2.45 g $\text{K}_2\text{Cr}_2\text{O}_7$ in 375 ml conc. HNO_3 (NO_2 -free) and 125 ml distilled water.

Test - 6 ml reagent and 2 ml acetone are mixed at room temperature. Blue or violet colour shows impurities. The mixture should be allowed to stand 15 mins. before reporting absence of colour.

(2) Permanganate Test

0.1 ml 0.1 N KMnO_4 and 10 ml acetone are mixed and allowed to stand in the dark for 16 hours. No decolourisation should be shown.

(3) Silver Test (Tollen's Test)

Reagent - AgNO_3 9 g, NaOH 6 g, ammonia (0.88) 60 ml, distilled water 240 ml. If any turbidity is noted, the solution should be filtered and if any further turbidity develops a fresh solution should be prepared.

Test - 10 ml acetone, 10 ml distilled water and 2 ml reagent are mixed and allowed to stand in the dark for 30 mins., and the turbidity measured on the Spekker using 3 cm. cells and neutral (grey) screens. If the Spekker reading is more than 0.05, the test is repeated with new reagent and, if confirmed, the acetone is rejected.

SECRET

G agents (cont'd.)

(e) By indole (1955)

PRINCIPLE

In the presence of peroxide and in controlled alkaline conditions, small quantities of G gases react with indole to produce a fluorescent compound. Larger quantities of G gases give dyes of the indigo type.

COLLECTION

As for G by dianisidine, viz. all-glass miniature bubblers charged with 2 ml of solvent (cyclohexanol containing 5% of ethylene glycol monomethyl ether) and operated at 1 litre per minute. The cyclohexanol should be of good quality, dry, and distil between 158 and 161°C.

REAGENTS

- (i) Isopropanol/water. A 1:1 mixture of AR isopropanol and distilled water. The distilled water should be boiled to expel carbon dioxide, if necessary, so that its pH is between 6.5 and 7.0, and then cooled before adding the isopropanol.
- (ii) Sodium perborate solution. 1 g sodium perborate in 100 ml water. This solution can be stored in the dark for up to 4 days.
- (iii) Indole solution. 1 g indole (white crystals) is dissolved in purified acetone. This solution if stored in the dark, is stable for about 1 week.

ANALYTICAL METHOD

The fluorimeter should be switched on 30 mins, before it will be required, and the setting of the neutral density wedge should be checked before commencing analysis, using a standard fluorescent solution and the standard reading on the "helipot" resistor, and moving the wedge if required.

The reagents are mixed in the proportions 23 ml i, 1 ml ii, and 1 ml iii, sufficient mixed reagent being prepared for about 20 samples and several blanks in one batch. The bubbler is made up to the mark (25 ml) with the mixed reagent, the inlet tube washed and the solution mixed as in the dianisidine method. Immediately after mixing, the solution is poured into the fluorimeter cell and placed in position in the instrument, and the "helipot" resistor is turned until a null point is shown on the galvanometer, the maximum reading recorded on the "helipot" being noted. The time from adding the mixed reagents to reaching the maximum reading is less than 2 minutes, so that there must not be any delay at this point. A blank test is made using the same reagents, but without any G agent.

The amount of G agent present is found by reference to a calibration curve, which should be prepared on the same day as that on which the samples are analysed.

NOTES: (1) The checking of the position of the neutral density wedge can be carried out using any suitable fluorescent solution. Among those actually used, have been:

Vaseline-xylene A fluorimeter cell is filled with a solution of vaseline in xylene, of such a strength as to give a suitable reading, the cell is covered with a cover slip and sealed with shellac to prevent evaporation. This solution deteriorates slowly and should be checked against another standard at intervals.

SECRET

Fluorescein A strong solution is reasonably stable, but the dilute solution required is stable only for a few hours and should be prepared by dilution from the strong solution at frequent intervals (4 or 5 times daily)

(2) A modified technique has been used occasionally for GB, in which the maximum reading is not obtained until about 10 mins. after adding the mixed reagents (which are varied from those used above) and is thus suitable for batch working. This is described in P.T.P. 272.

CALIBRATION

A typical calibration is:-

µg GB	0.0	4.17	8.34	12.51	16.68
Reading	33	127	235	337	440

When it is desired to measure amounts of 0.4 µg GB, a more dilute solution would be employed than was used in obtaining the results quoted above.

SECRET

22. HYDROGEN CYANIDE

(a) Macro Method (1954)

PRINCIPLE

The Liebig method of titration with silver nitrate is employed.

COLLECTION OF THE SAMPLE

Samples are collected in bubblers charged with Normal caustic soda solution.

REAGENTS

(i) 0.1 N AgNO_3

(ii) 0.02 N AgNO_3

ANALYTICAL METHOD

The sample is washed into a beaker flask and titrated direct with either 0.1 N AgNO_3 or 0.02 N AgNO_3 to the first trace of turbidity. The end-point is made sharper by adding a crystal of potassium iodide to the solution.

1 ml 0.02 N AgNO_3 = 0.00108 g HCN

(b) Micro Method (1954)

This has been described under Cyanide (see previous pages).

SECRET

23. INSECTICIDAL SMOKES

(a) DDT and BHC

(i) By hydrolysable chlorine content (1952)

PRINCIPLE

The method depends on the dehydro-halogenation of the insecticide by boiling with alcoholic potash, the chloride being estimated potentiometrically.

COLLECTION OF THE SAMPLE

The samples are taken in filters fitted with two layers of No. 1 Whatman filter paper.

REAGENTS

- (i) AR benzene (dry)
- (ii) AR 3% alcoholic potash
- (iii) Chloride-free distilled water
- (iv) 5% AR acetic acid
- (v) 0.002 N silver nitrate
- (vi) Absolute alcohol (chloride free).

METHOD

The papers are removed from the filter and extracted with dry benzene in a Soxhlet for half an hour. The benzene is then distilled off down to about 3 ml. 5 ml 3% alcoholic potash and 25 ml absolute alcohol are then added, and the mixture refluxed for 20 mins., the solution afterwards being evaporated to about 5 ml.

After cooling, a few ml of chloride-free distilled water are added, followed by 5 ml of 5% acetic acid and the solution washed into the special titration cell. The chloride is then titrated with 0.002 N AgNO_3 as described previously (see Chloride).

CALIBRATION

1 ml 0.002 N AgNO_3 = 0.071 mg Cl⁻

The appropriate conversion to mg DDT or Gammaxane is then made according to the hydrolysable chlorine content of the sample. (Although DDT contains 5 atoms of chlorine in the molecule, only one of these is hydrolysable, representing about 10% of the weight of the molecule. In the case of BHC, three chlorine atoms are removed on hydrolysis with alcoholic potash giving a hydrolysable chlorine content of 36.6%).

The impurities present in technical samples will also contain hydrolysable chlorine, and this method is accurate only to the extent that the impurities are present in the smoke in the same proportion as in the original sample.

SECRET

Notes

(1) A blank (2 papers) should be extracted and treated in the same way as the samples, and this blank value allowed for.

(2) Heavy samples tend to block the filter paper and care must be taken to ensure that the flow rate is constant throughout the sampling period.

(3) It is important that the alcoholic solution should not be evaporated below about 5 ml, otherwise the molecule may break up further, and erroneous results be obtained.

(ii) By Polarograph

(1) HHC (1954)

COLLECTION OF THE SAMPLE

As above.

METHOD

The sample is extracted as above but using alcohol instead of benzene, and the extract is dissolved in a solution of 1% potassium chloride and 0.1% gelatine in 50/50 ethanol/water. A suitable aliquot of not more than 5 ml is placed in a previously calibrated cell containing a quiet mercury pool and a saturated calomel element (Doran dip type).

After de-oxygenation, a polarogram is taken between -0.5v and -1.6v, the wave height and sensitivity noted and the result read off from the calibration curve. A calibration between 0.001% (50 µg) and 0.01% (500 µg) has been shown to be linear.

(2) DDT

COLLECTION

As above.

METHOD

The papers are extracted in a Soxhlet with alcohol for half an hour, the alcohol then distilled off almost to dryness. The extract is dissolved in a solution consisting of 60% isopropanol and 40% of 2.5% tetramethylammonium citrate in water and containing a trace of gelatine. A suitable aliquot of not more than 5 ml is placed in the cell with a dropping mercury electrode and a quiet mercury pool.

After de-oxygenation, a polarogram is taken between -0.5v and -1.6v, the wave height and sensitivity noted and the result read off on the calibration curve.

A calibration from 0.01% to 0.02% has been prepared.

The technique used above for Gammexane with the quiet mercury pool replacing the dropping mercury electrode and also using a saturated calomel electrode, may also be more convenient for DDT, but has not been tested.

SECRET

INSECTICIDAL SMOKE (cont'd.)

(b) DNOC (pre 1946)

PRINCIPLE

Caustic soda reacts with DNOC to give a distinctive colour reaction.

COLLECTION OF THE SAMPLE

Samples are taken on No.1 Whatman filters as described for DDT.

REAGENTS

- (i) Absolute alcohol
- (ii) 5% NaOH (freshly prepared)

ANALYTICAL METHOD

The samples are extracted in Soxhlets with absolute alcohol, and, after cooling, are made up to a known volume with alcohol. A suitable aliquot portion of the extract, containing between 0.05 and 1.0 mg DNOC, is diluted to 10 ml in a dry tube with absolute alcohol.

1 ml 5% aqueous sodium hydroxide is added and the colour read off immediately in the Spekker, using No.7 dark blue filters.

TYPICAL CALIBRATION

mg DNOC	0.05	0.10	0.20	0.40	0.60	0.80
Spekker Reading	0.15	0.25	0.43	0.63	0.77	0.88

Notes

- (1) Clean redistilled industrial spirit may be used for the extraction instead of absolute alcohol if the calibration curve is made with the same solvent.
- (2) An iodimetric method for DNOC is given in Ministry of Agriculture and Fisheries Technical Bulletin No.1, but this has not been tested at Porton.

SECRET

24. MANGANESE SULPHATE

USE

Manganese sulphate solution has been used as a substitute weapon charging, in cases where it was desired to use only a very small amount of charging and therefore great sensitivity was required in the analytical method.

PRINCIPLE OF THE METHOD

The manganese is oxidised to permanganic acid which is then reacted with tetramethyldiaminodiphenylmethane to give a blue colour.

COLLECTION OF SAMPLE

Samples are collected at approximately 1 l/min. in all-glass miniature bubblers, charged 5 ml special distilled water (see below). The bubblers and all glassware are prepared for use by washing first with dilute hydrochloric acid, then with tap water, and finally with special distilled water.

ANALYSIS.

Reagents

All reagents are purified to be free of manganese.

- (i) Glass-distilled water is used in all operations, and for final washing of glassware.
- (ii) Tetramethyl diaminodiphenyl methane ("Tetrabase") 1% solution in acetone, prepared fresh daily.
- (iii) Saturated solution of potassium periodate in water, prepared fresh daily.
- (iv) Redistilled glacial acetic acid.
- (v) Buffer solution:

100 g sodium acetate	} dissolved in 540 ml water.
4 g sodium phosphate	
4 g calcium chloride	
5 g sodium carbonate	
5 g sodium bicarbonate	

20 g calcium carbonate are added, and the whole is autoclaved at 120°C for $\frac{3}{4}$ hour.

The mixture is filtered hot, and the filtrate made up to 1 litre. 50 ml of the solution is titrated with glacial acetic acid in a pH meter to pH 4.8. The calculated amount of glacial acetic acid is then added to the whole bulk to bring it to this pH.

METHOD

4 ml acetate buffer is added to the sample in the bubbler, and the inside of the stem is washed by blowing into the side arm so as to force the liquid up the stem. This operation is repeated to ensure that any manganese salt impinged on the inside of the upper part of the stem is washed into the bubbler. The stem is removed and drained as far as possible, and the contents of the bubbler mixed with a glass rod plunger. The bubbler is placed in an ice-water bath for 10 minutes, then 0.5 ml potassium periodate solution is added and mixed.

SECRET

1 ml 0.1% solution of tetrabase in acetone is added, the solution again mixed and the colour read at maximum development in a Spekker Absorptionmeter using Spectrum Yellow 606 filters. A 1 cm, or $\frac{1}{4}$ cm, cell is used according to the apparent depth of colour obtained.

If a reading in excess of 0.8 in the $\frac{1}{4}$ cm. cell is expected, an aliquot portion must be taken, diluted to 5 ml with water, and treated as above.

TYPICAL CALIBRATION

µg Manganese	0.0	0.025	0.038	0.063	0.10	0.20	0.30
Spekker Reading 1 cm. cell	0.03	0.105	0.135	0.25	0.32	0.595	0.86

µg Manganese	0.20	0.40	0.60	0.80	1.00	1.50	2.00
Spekker Reading 0.25 cm. cell	0.145	0.26	0.37	0.445	0.50	0.635	0.72

NOTES

- (1) When the smaller size Spekker cell is used the calibration is a curve and not a straight line.
- (2) In view of the extreme sensitivity of this method, it was found advisable to spray the whole layout with water before the trial to reduce the possibility of dust being sampled. The bubblers were also protected by filter paper caps until immediately before the trial. Also, in order to reduce the risk of extracting manganese from the glass, the bubblers were not charged until the day of the trial.
- (3) A method developed by J.A. Adam (Chemical Inspectorate Report No.72) using leuco malachite green instead of tetra-base, has several advantages over the above method.

The buffer is simpler and does not require tedious processing, including autoclaving and the colour develops to a maximum, which is stable for at least 10 mins., whilst in the above method a fleeting maximum has to be observed and measured. As recommended by Adam, the range of concentrations of manganese measured by the method is very similar to that of the Porton test, but the method can be made even more sensitive by reducing the total volume used and reducing the strength of the buffer solution, as given below:-

REAGENTS

- (i) Buffer. 25 ml of Analar acetic acid and 8.2 grams anhydrous 'Analar' sodium acetate made up to 1 litre.
- (ii) Periodate. 0.115 g potassium periodate in 50 ml.
- (iii) Leuco base, 0.05 g Leuco Malachite Green dissolved and made up to 50 ml in acetone.

METHOD

To the sample of manganese in 5 ml special distilled water, 2 ml of buffer are added, mixed, then 1 ml of periodate is added and mixed, and the sample allowed to stand for 5 mins. Then 0.2 ml of leuco base solution is added and mixed and allowed to stand for a further 30 mins. before the colour is read in the Spekker, using the 1 cm cell and the Ilford 607 orange filters.

SECRET

The following calibration curves were obtained:

$\mu\text{g Mn}$	"Spekker Reading"				Mean
0.0	18.5	22	19	20.	20
0.01	39.5	43	38.5	41.5	40.6
0.02	53.	62.5	57.	56.5	57.2
0.03	81.5	85	83.	78.	81.9
0.04	99.5	103.5	100.5	94.	99.4
0.05	119.5	118.	116.	112.5	116.5

For samples expected to contain more than 0.05 $\mu\text{g Mn}$ either aliquoting, or reverting to the use of the stronger buffer solution would be necessary.

With this extreme sensitivity, greater care must be taken with regard to the cleanliness of apparatus, the purity of reagents and distilled water, and the prevention of contamination of the samples by dust, etc.

SECRET

25. METHYL ACETOACETATE (1954)

USE

Methyl acetoacetate (MAA) has very similar physical properties to GB and is used as a substitute.

PRINCIPLE OF THE METHOD

The methyl acetoacetate is coupled with diazotised 2,5 dichloroaniline and made alkaline to give a brownish colour.

COLLECTION OF THE SAMPLE

MAA vapour is sampled at 1 litre per minute in miniature bubblers charged with 5 ml of water. The "slip" is 5% for 10 minute sampling periods at 60°F.

REAGENTS

(i) Diazo solution: 4.6 g 2,5 dichloroaniline and 6 ml of conc. HCl are placed in a 100 ml beaker, 5 ml of water added and warmed gently until the whole of the base is converted into hydrochloride (a white paste). This is stirred gently with a glass rod, a further 20 ml of water added, heated and stirred till all the hydrochloride has dissolved. The solution should be pale straw coloured. It is cooled rapidly with stirring in an ice and water bath to below 15°C, and a solution of 1 g sodium nitrite in 5 ml of water added. The nitrite solution should be added quickly with stirring and not allowed to touch the sides of the beaker, or back coupling will occur. The solution is filtered from traces of insoluble matter into a dark brown bottle and stored in a cool place out of direct light. The solution should remain stable for at least 4 hours.

(ii) Isopropanol - NaOH, 220 ml isopropanol, 100 ml N NaOH and 90 ml water are mixed and stored. The solution becomes discoloured on standing in contact with rubber; hence rubber connections should be kept to a minimum.

SPECIAL APPARATUS

The isopropanol - NaOH reagent is charged into the apparatus shown in Fig. 28.

ANALYTICAL METHOD

0.5 ml of diazo solution is added to the bubbler contents from a pipette, and mixed.

20 ml of the isopropanol - NaOH reagent is added as quickly as possible from the special automatic pipette, and mixed. The first filling of this pipette should be run to waste to clear any reagent that has been in contact with rubber. The glass tube extension is fitted into the bubbler to deliver the isopropanol - NaOH solution to the bottom of the bubbler. The pipette emptying tap is opened with one hand to discharge the contents rapidly into the bubbler and the bubbler is moved quickly up and down immediately afterwards, using the other hand.

SECRET

The red colour obtained is read on the Spekker Absorptiometer using the spectrum blue 603 filters, against a blank solution prepared from 5 ml of water, 0.5 ml of diazo solution, and made up with isopropanol - NaOH from the automatic pipette. Readings are made 1 minute after addition of the reagents, using the appropriate Spekker cell according to the colour.

If the colour is too deep to be read in the 0.25 cm cell (i.e. over 700 µg MAA) the 0.25 mm cell can be used and the range extended up to about 10,000 µg MAA. With these greater quantities, however, the reaction does not obey the Beer-Lambert law and the amount of MAA has to be found by reference to a calibration curve (which is not linear).

CALIBRATION

Typical results are as follows:-

µg MAA	7	14	28	57	85	143	285	428	574
Nett Spekker	3 cm								
	0.115	0.23	0.45	0.89					
Reading	1 cm								
			0.16	0.33	0.46	0.80			
	0.25 cm								
						0.20	0.41	0.59	0.79
µg MAA	1,400	2,800	4,200	5,600	8,400				
Spekker Reading	0.20	0.39	0.55	0.68	0.84				
0.25 mm cell									

Notes (1) The accuracy of the method depends on the technique of adding the reagents and mixing the solution, and operators should always have some practice in the analysis using known samples before proceeding to examine samples from a trial.

(2) If any apparatus which has been used for MAA is to be used for G agents, very special care should be taken to wash it thoroughly, since a trace of MAA interferes seriously with the analysis of G agents by the dianisidine method.

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SECRET

26. METHYL SALICYLATE (1948)

USE

Methyl salicylate has been used as a substitute for mustard gas.

PRINCIPLE

When phospho-tungsto-molybdic reagent is added to a phenol and treated with sodium carbonate, a blue colour is produced, proportional to the amount of phenol present.

COLLECTION OF THE SAMPLE

Samples are collected in bead bubblers containing 15 ml 0.1 N NaOH.

In some cases a filter is fitted in front of the bubbler to exclude dust, and in these cases, sampling is continued after the cloud has passed to ensure that any droplets of methyl salicylate have evaporated and are not left on the filter in droplet form.

REAGENTS

(i) 0.1 N NaOH (0.4% solution)

(ii) Phenol reagent: 100 g sodium tungstate (Na_2WO_4) and 25 g sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) are dissolved in 700 ml water. 50 ml syrupy (85%) phosphoric acid and 100 ml conc. HCl are added, and the mixture refluxed for 10 hours using a reflux condenser with a ground glass joint. 150 g lithium sulphate, 50 ml water and a little bromine are added and the mixture boiled for 15 mins. to remove excess bromine. It is then cooled and diluted to 100 ml.

The reagent is yellow, but should not have any green tinge.

(iii) Sodium carbonate solution: 15 g Na_2CO_3 (anhydrous) in 100 ml water.

ANALYTICAL METHOD

An aliquot of the sample (containing not more than 0.1 mg ME) is transferred to a tube and made up to 10 ml with 0.1 N NaOH if necessary.

1 ml of the phenol reagent is added and mixed, then 3 ml 15% sodium carbonate and mixed again. The tube is then placed in a water bath or incubator at about 37°C for 20 mins. The blue colour is read on the Spekker using the No. 2 red filters. A blank determination using 10 ml of the same 0.1 N NaOH and all the other reagents is made with each batch of determinations and the difference between the two readings referred to the calibration.

Notes (1) Sufficient 0.1 N NaOH should be prepared to fill the bubblers and carry out the analysis, i.e. the whole procedure should be carried out with the same solution.

(2) The solution should be mixed with a glass rod; the thumb should not be placed over the tube.

CALIBRATION

A fresh calibration curve should be prepared for each batch of phenol reagent. Since this reagent deteriorates slowly with storage, a few points on the calibration curve should also be checked with each batch of determinations.

SECRET

27. MUSTARD GAS

(a) By DB-3 (1954)

PRINCIPLE OF THE METHOD

The active alkyl halogen group of mustard gas couples with DB-3 (p-nitrobenzyl pyridine) to give a blue or violet colour when made alkaline.

COLLECTION OF THE SAMPLE

All-glass miniature bubblers charged with 5 ml of cyclohexanol, containing 5% methyl cellosolve and operated at 1 litre/min. are used.

The slip varies with the time and temperature of sampling as shown in the table:

Temperature °F	% Slip			
	Time of Sampling (mins.)			
	15	45	60	120
70	3	5	5	7
90	3	5	7	10

REAGENTS

- (i) Cyclohexanol, containing 5% methyl cellosolve.
- (ii) Absolute alcohol.
- (iii) 10% w/v DB-3 in absolute alcohol.
- (iv) Buffer solution: 0.33 g phthalic acid and 3 ml N NaOH solution in 100 ml of solution.
- (v) Perchlorate buffer. To 100 g of recrystallised sodium perchlorate[®] 50 ml buffer solution is added, the mixture warmed to room temperature and then diluted to 100 ml with water.
- (vi) Piperidine.

ANALYTICAL METHOD

Immediately prior to analysing a batch of samples, a "mixed reagent" is prepared in the following proportions by volume:

- 2.5 ml cyclohexanol
- 7.5 ml absolute alcohol
- 2.0 ml DB-3 solution
- 2.0 ml perchlorate buffer

It is found convenient to process the samples in batches of 30, in which case the above quantities should be multiplied by 35 to allow for wastage.

SECRET

To each bubbler, 14 ml of the "mixed reagent is added from an automatic pipette, the bubbler stem washed in the bubbler contents by repeated dipping and draining, and the solution then thoroughly mixed by means of a plunger stirrer, which is left in the bubbler for further use.

The bubbler is then placed in a water bath thermostatically controlled at 80°C for 30 minutes, cooled by standing in a cold water bath, 1 ml of piperidine is added, the contents are well mixed by means of the glass rod plunger and the resultant colour is measured immediately in the Spekker absorptiometer using the Spectrum Yellow 606 screens and the appropriate cell, either 30 mm, 10 mm, 5 mm or 2.5 mm according to the depth of colour.

If the colour is too deep for the 2.5 mm cell, (i.e. the dosage (Ct) is over 550 ng.min/m²) the colour can be read using the special 0.25 mm capillary cells (these capillary cells have a detachable front surface which is removed for cleaning and refilling, and are supplied by Messrs. Tintometer Ltd. of Salisbury). With these cells, the Spectrum Yellow 606 screens can be used for readings corresponding to dosages up to about 6,000 ng.min/m². Should the amount of mustard gas in the sample be even greater than this, the Spectrum Red 608 screens can be used for dosages up to about 16,000 ng.min/m², but in this case the amount of H will have to be found by reference to the calibration curve.

A certain amount of practice is required in filling the capillary cells quickly, before the colour begins to fade; hence, if high results are expected from any trial, all operators should carry out calibration curves with these cells before analysing the samples.

- NOTES: (1) If the perchlorate has not been efficiently recrystallised, both this solution and the mixed reagent may require filtration before use.
- (2) The mixed reagent must be prepared for each batch of samples; it must not be stored mixed.
- (3) The final volume of 20 ml was chosen because this is just sufficient to fill the 30 mm cell of the Spekker, and also, with this volume, the liquid level in the bubbler is below the level of the water in the thermostat bath.

CALIBRATION

A solution of pure mustard gas in cyclohexanol is prepared (e.g. 0.5 g in 50 ml) and subsequent dilutions from this are made with 50/50 cyclohexanol/absolute alcohol mixture. The stability of mustard gas in cyclohexanol has been found to be good for several days and that in the cyclohexanol/absolute alcohol good for 24 hours.

Aliquots for the calibration are measured from a microburette into all glass bubblers, diluted to 15 ml with cyclohexanol/absolute alcohol, 2 ml of DB-3 solution and 2 ml of perchlorate buffer solution added, then stirred, and the procedure carried out as above.

A set of typical results, using the four different sizes of Spekker cell with the Spectrum yellow 606 screens, is as follows:

SECRET

30 mm Cell		10 mm Cell		5 mm Cell		2.5 mm Cell	
µg H	Reading	µg H	Reading	µg H	Reading	µg H	Reading
0.0	0.07	0.0	0.02	0.0	0.01	0.0	0.0
8.9	0.28	26.8	0.235	53.5	0.215	107	0.215
17.8	0.235	53.5	0.43	107	0.41	214	0.405
26.8	0.645	80.3	0.615	161	0.595	321	0.58
35.7	0.845	107.	0.82	214	0.795	401	0.77
44.6	1.01	134.	1.02	241	0.91	428	0.78
53.5	1.22	161.	1.19	321	1.15	535	0.94
Factor	46.5		44.5		45.0		45.7
Average conversion factor 45.4							

The conversion factor is the amount by which the Spekker reading must be multiplied to give µg H, and for the 10 mm, 5 mm and 2.5 mm cells has been calculated back to the 30 mm cell depth.

A set of typical results using the capillary cells is given below together with a calibration done at the same time with the same reagents but using a more dilute solution of mustard gas and the 3 cm cells. With these reagents the results for the 3 cm cells were different from those quoted above. This discrepancy brings out the need for recalibration with each new batch of reagent.

Spectrum Yellow 606 screens				Spectrum Red 608 screens	
3 cm cells		0.25 mm Cell		0.25 mm Cell	
µg H	Reading	µg H	Reading	µg H	Reading
0.0	0.08				
9.5	0.245	1260	0.18	3150	0.17
19	0.41	1520	0.365	6300	(0.285
					(0.305
28.5	0.555	3780	0.535	9450	0.385
38	0.715	5040	0.695	12600	0.485
47.5	0.90	6300	0.835	15750	0.56
57	1.025				
Factor	60	7100		No factor - curve	

It is noted that the calibration with the 0.25 mm cells and the yellow 606 screens gives a straight line up to about 6,000 µg H and the factor in this case - 7100 - is (within the limits of experimental error) proportional to that for the 3 cm cells (60) i.e. $60 \times 120 = 7200$.

Thus, the colour obeys Beers Law over the whole range of concentrations from 5 to 6,000 µg H and the appropriate cell may be used with the same factor (corrected for cell size) throughout.

With the Spectrum Red 608 screens the calibration points lie on a curve so that a conversion factor cannot be applied and reference must be made to the curve for each result.

References O.S.R.D. 4288
 P.T.P. 380

APPENDIX
WORKING WITH THE CELL

3. BY STANDARDIZATION METHOD

PREPARATION OF THE CELL

The standard gas is measured with volume burette. The gas is measured at the end point is indicated either by electrometric method or by colorimetric method. The gas can be measured very rapidly.

4. BY ELECTROMETRIC METHOD

The measurement of cell, silver, bromine, etc. is done by the method as described in the standardization method. The gas is measured at the end point is indicated either by electrometric method or by colorimetric method. The gas can be measured very rapidly.

Electrodes: The electrodes for the titration of O_2 are prepared by the method as described in the standardization method. The gas is measured at the end point is indicated either by electrometric method or by colorimetric method. The gas can be measured very rapidly.

Once prepared, the electrodes must never be allowed to dry. They should be kept immersed in their respective cell solutions. The electrodes should be cleaned and prepared, by immersing for a few minutes in dilute acid (conc.) and then washing well with distilled water. The electrodes should be kept immersed in dilute acid (1:1 conc. H_2SO_4 and 1:1 conc. HCl). The silver electrode should be cleaned by polishing with the emery paper.

After cleaning the electrodes, it is desirable, if possible, to assemble the cell, and leave the electrodes connected together through the galvanometer for several hours. During this, several titrations using a standard solution of standard gas may have to be done before the electrodes are in a stable condition.

CONNECTION OF THE CIRCUIT

The sample is taken at 1 litre per minute through two all-glass miniature bubblers in series, each charged with 5 ml of 50% acetic acid.

REAGENTS

- (i) Silver cell - 0.1 N silver nitrate (for the electrometric method only)
- (ii) Bromine solution - A saturated solution of pure bromine in 0.1 N hydrochloric acid is prepared by shaking and allowing to stand.
- (iii) Dilute bromine solution for titration - 1 ml of the saturated bromine solution, as above, is diluted to 200 ml with dilute acid (10 ml conc. H_2SO_4 and 1.5 ml conc. HCl in 2 litres water). This solution should be prepared freshly and not used if more than 3 hours old.

ANALYTICAL METHOD

The sample is poured into the titration cell, and the bubblers washed out with distilled water which is added to the sample. Bromine solution is added slowly from the burette until either the methyl red is decolorised, or the galvanometer spot suddenly shows a wide and rapid deflection.

SECRET

MUSTARD GAS (cont'd.)

(b) By titration with bromine (1954)

PRINCIPLE OF THE METHOD

The mustard gas is titrated with dilute bromine and the excess of oxidising agent at the end point is indicated either by decolourisation of methyl red, or electrometrically. Results can be obtained very rapidly.

APPARATUS AND ELECTRODES (for electrometric method only)

The arrangement of cell, stirrer, galvanometer, and burette is exactly the same as that already described in the potentiometric method for the determination of chloride, except that the shorting switch and resistance between the electrodes and the galvanometer is omitted.

Electrodes: The electrode in the titration cell consists of a small piece of platinum foil, 4 x 4 mm, welded on to a platinum wire lead on the end of a glass tube in the conventional manner. A little mercury is placed in the glass tube to make contact between the platinum foil and the wire leading to the galvanometer. The reference half-cell consists of a piece of pure silver rod immersed in 0.1N silver nitrate solution.

Once prepared, the electrodes must never be allowed to become dry, but must be kept immersed in their respective cell solutions. The platinum electrode should be cleaned and prepared, by immersing for a few minutes in boiling nitric acid (conc.) and then washing well with distilled water. It should then be kept immersed in dilute acid (10 ml conc. H_2SO_4 and 1.5 ml conc. HCl in 2 litres). The silver electrode should be cleaned by polishing with fine emery paper.

After cleaning the electrodes, it is desirable, if possible, to assemble the cell, and leave the electrodes connected together through the galvanometer for several hours. Failing this, several titrations using a standard solution of mustard gas may have to be done before the electrodes are in a usable condition.

COLLECTION OF THE SAMPLE

The sample is taken at 1 litre per minute through two all-glass miniature bubblers in series, each charged with 5 ml of 50% acetic acid.

REAGENTS

- (i) Silver cell - 0.1 N silver nitrate (for the electrometric method only)
- (ii) Bromine solution - A saturated solution of pure bromine in 0.1 N hydrochloric acid is prepared by shaking and allowing to stand.
- (iii) Dilute bromine solution for titration - 1 ml of the saturated bromine solution, as above, is diluted to 200 ml with dilute acid (10 ml conc. H_2SO_4 and 1.5 ml conc. HCl in 2 litres water). This solution should be prepared freshly and not used if more than 3 hours old.

ANALYTICAL METHOD

The sample is poured into the titration cell, and the bubblers washed out with distilled water which is added to the sample. Bromine solution is added slowly from the burette until either the methyl red is decolourised, or the galvanometer spot suddenly shows a wide and rapid deflection.

SECRET

CALIBRATION

A calibration curve should be drawn for each new batch of dilute bromine solution, using a standard solution of mustard gas in 50% acetic acid and titrating measured amounts. There is usually a small blank on the acetic acid. Typical results are:-

mg "H"	0.0	0.05	0.10	0.20	0.30	0.40	0.50
ml Br soln.	0.25	0.55	0.85	1.50	2.13	2.75	3.35

Note:

The method is not specific and any reducing agent will interfere. Trouble has been experienced when using bubblers with rubber bungs, from traces of rubber from the bungs.

References: O.S.R.D. 401
C.D. (Aust.) 68

SECRET

MUSTARD GAS (Cont'd.)

(c) By chloride titration after absorption on silica gel or on charcoal (Pre 1946)

PRINCIPLE

The solid absorbent in the plastic tube gives a very convenient way of taking large numbers of samples. Silica gel was found satisfactory in England, but with the higher temperatures and humidities in the tropics, the gel absorbed so much water that the slip of mustard gas through the tubes was excessive. Charcoal was found to be more suitable for tropical use. However, charcoal retains some of the H permanently, so that dosages of less than 50 mg.min/m³ were doubtful and for those above 50 a combined slip and absorption correction factor of 1.43 had to be applied.

The gel or charcoal is extracted with potassium nitrate solution and this extract titrated potentiometrically for chloride (see above). The method is non-specific.

Reference P.R. 2664

SECRET

MUSTARD GAS (Cont'd.)

(d) By iodo-platinate

PRINCIPLE

The mustard gas is collected in bubblers containing 50% acetic acid. This solution liberates iodine from sodium iodo-platinate, the iodine being determined colorimetrically with starch.

References P.M. 19

Suffield Technical Minute 97

to

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SECRET

28. NICKEL (1950)

USE

Nickel is used as a characteriser in methyl salicylate when there is a risk of decomposition of an organic characteriser.

PRINCIPLE

The sample is treated by a wet oxidation process, basified with ammonia and filtered. A suitable aliquot is then treated with dimethylglyoxime and the red colour measured.

COLLECTION

Crater samples These will normally consist of sand or earth.

Area samples May consist of felt pads or turves.

REAGENTS

- (i) Conc. nitric acid.
- (ii) Ammonium hydroxide.
- (iii) 1% Dimethylglyoxime solution in ethanol.
- (iv) Bromine water.

ANALYTICAL METHOD

Sand samples

A suitable weight of the sand according to the contamination (e.g. for 25 pr. shell - 10 g for skimmed samples and 30 g for deep crater samples), is accurately weighed into a small (50 ml) Kjeldahl flask. Conc. nitric acid, 5 ml for each 10 g of sand, is then added and the mixture boiled for 3 - 5 mins. with vigorous shaking. The mixture is then diluted with 5 ml water, cooled, made strongly alkaline with ammonia and filtered through a Buchner funnel fitted with a No. 1 Whatman filter paper coated with a little "Celite" filter aid. The filtrate is transferred to a 50 ml cylinder and with washings made up to 50 ml. A suitable aliquot portion is taken, 3 ml of 0.880 ammonium hydroxide added, diluted to 40 ml with water, and 1 ml of 1% dimethyl glyoxime in ethanol added with stirring. A few drops of bromine water are then added, the volume made up to 50 ml with water and allowed to stand for 5 mins.

The colour is measured on the "Unicam" SP.350 Spectrophotometer at a wave length of 520 mμ (A). A similar aliquot without the addition of any reagents is diluted to 50 ml and its colour measured to give the blank (B). The weight of nickel is then calculated from the difference between readings A and B, by reference to the calibration curve.

Felt Pads

The felt pad is extracted with chloroform. This should be done as soon as possible or resinification of the nickel compound may take place. The chloroform is evaporated off, 5 ml of nitric acid added and the mixture heated to 100°C and then transferred to a small Kjeldahl flask with further washings of hot nitric acid. The acid is evaporated down, sulphuric acid added and the heating continued till the oxidation is complete. The liquid is then cooled, diluted, made ammoniacal and treated as above.

SECRET

Calibration Curve

0.6730 g $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is made up to 1 litre, 10 ml of this solution diluted to 100 ml, then aliquots of 1 to 5 ml of this dilute solution transferred to 50 ml measuring cylinders and the colour developed as above.

Determination of Nickel in the Shell Charging

A suitable amount of charging (0.5 g) is accurately weighed into a small weighing bottle and transferred by means of chloroform to a 100 ml beaker. The chloroform is carefully evaporated off, conc. nitric acid is added, the mixture boiled for 3 mins., and then diluted to 1 litre and the nickel determined as already described.

SECRET

29. NITROGEN MUSTARDS

The nitrogen mustards can be estimated by the use of DB-3.

The method used previously was to sample the vapour through bubblers containing an acidified solution of DB-3 in cellosolve and ethylene glycol, but is it considered that a method similar to that used for mustard gas (see above) would be more suitable. The time of heating the solution would probably have to be longer for HN than for H and precise details would have to be worked out.

SECRET

30. NITROUS FUMES (1950)

PRINCIPLE

The method is based on the formation of a diazo compound by the action of nitrous acid, liberated from the nitrite in acid solution, with sulphanilic acid and the coupling of this compound with anaphthylamine to give a violet colour.

COLLECTION

No satisfactory absorbent for use in bubblers exists and samples are collected in evacuated bottles to which 15 ml of "nitrite free" sodium hydroxide 5% aqueous solution is added before evacuating. The sides of the bottle are wetted with this solution before and again after sampling, and the bottle is allowed to stand for at least 15 mins. before analysis if the sample is mainly NO₂ and for 5 hours if NO is expected to be present. (With NO at 1 in 100,000 90% oxidation occurs in 5 hours).

If samples are required from inaccessible points, a length of fairly small bore tubing is used between the bottle and the sampling point. This is cleared by taking a sufficient number of strokes with a suction pump immediately before connecting to the evacuated bottle and taking the sample.

REAGENTS

- (i) Glacial acetic acid.
- (ii) Anaphthylamine - 0.25 g in 150 ml dilute acetic acid (70 ml glacial acetic acid + 500 ml water).
- (iii) Sulphanilic acid 1.25 g in 150 ml dilute acetic acid (as above).

Solutions (ii) and (iii) should be stored separately, but can be mixed together in equal proportions on the day of use.

METHOD

The liquid is transferred from the bottle to a graduated flask (50 ml size if the sample is expected to be small, 100 ml otherwise), the bottle is washed out and the washings added to the flask. The volume is then made up to the mark.

In a 25 ml graduated flask are placed 2 ml of the mixed reagent((ii) and (iii) above), 2.5 ml glacial acetic acid, a suitable aliquot of the sample, and water to make up to 25 ml.

The mixture is shaken, allowed to stand for 20 mins., transferred to the Spekker cell and the colour intensity measured using the green filters No. 604.

CALIBRATION

An aqueous solution of sodium or potassium nitrite is prepared containing 0.001 mg NO₂ radical per ml and suitable aliquots used. Separate curves should be prepared for the 3 cm., 1 cm. and 0.25 cm cells.

Blank readings should be carried out on the "nitrite free" sodium hydroxide used as the absorbent.

Note: Nitrogen peroxide reacts with sodium hydroxide to give an equimolecular mixture of nitrite and nitrate.

SECRET



Hence the weight of NO_2 gas present initially is double the weight of nitrite radical measured.

Typical curve - 3 cm cell.

mg NO_2 (gas)	0	0.004	0.008	0.016	0.020
Spekker Reading (3 cm cell)	0.03	0.185	0.305	0.505	0.585

Note: This method could probably be improved - cf. Analyst 1951, vol. 76, p.599.

SECRET

31. PHENYL α -NAPHTHYLAMINE NAP (pre - 1946)

USE

NAP is used as a characteriser in the estimation of droplets. It is more soluble than most dyes in many agents, and, being a dye intermediate, it is also more sensitive. Its chief use to date has been in the estimation of droplets collected on cascade impactor slides.

PRINCIPLE

The phenyl α -naphthylamine is coupled with diazotised sulphanilic acid and the colour measured.

COLLECTION OF SAMPLE

NAP is used mainly for samples collected on cascade impactor plates.

REAGENTS

- (i) Diazotised sulphanilic acid solution - 2 g AR sulphanilic acid dissolved in water to which 5 ml 2 N NaOH has been added is made up to 100 ml with water. This is cooled in an ice bath to below 5°C, then 6 ml conc. HCl is added, followed by the slow addition of a solution of 0.8 g AR sodium nitrite in 20 ml water with constant stirring. This solution should be stored in a dark bottle in a cool place and should not be kept for more than 5 days.
- (ii) Dilute hydrochloric acid (1 vol. conc. HCl: 1 vol. water).
- (iii) Alcohol (at least 95% ethanol).

METHOD

- (1) For heavily contaminated slides - as is usual for the first and second slides from the impactor.

The slide is held by the edges, contaminated side uppermost and several drops of alcohol from a dropping pipette allowed to flow on to the contaminated part. This is well mixed with the aid of the tip of the pipette and allowed to run off the slide through a small funnel into a 10 ml graduated flask. This is repeated with several lots of alcohol, keeping the total volume of the washings below 8 ml. 1 ml diazotised sulphanilic acid solution, and 1 ml dilute HCl solution are then added, the volume made up to 10 ml with alcohol, well shaken and the colour measured on the Spekker using the 1 cm cell and the No.5 green filters.

- (2) For lightly contaminated slides e.g. the third and fourth slides from an impactor, the technique is modified to give a smaller volume of solution.

A special dropping pipette is used which has its end drawn out to a capillary about 1 mm in diameter and 8 or 9 cm long. The contamination is well mixed with a few drops of alcohol by means of the tip of the capillary, and is then sucked into the pipette and transferred to a 2" x $\frac{1}{4}$ " test tube which has been drawn out and graduated at the 0.5 ml mark.

SECRET

This washing is repeated several times, taking care that the total volume does not exceed 0.3 ml. To this is added 3 drops of diazotised sulphanilic acid solution and 4 drops of the dilute HCl. The volume is made up to 0.5 ml with alcohol and mixed by immersing the capillary of the pipette and slowly bubbling air through the solution. The solution is then transferred by means of the pipette to the 1 cm (0.5 ml) micro cell and the colour measured in the Spekker. For dirty samples it is necessary to centrifuge the solution before transferring it to the Spekker cell.

CALIBRATION CURVE

The calibration curve should be prepared from the actual charging in the usual manner. Separate curves are required for each type of Spekker cell.

SECRET

32. PHOSGENE (1952)

PRINCIPLE

The phosgene is hydrolysed and the chloride titrated potentiometrically.

COLLECTION

Samples are taken in miniature bubblers containing 2 ml of alkaline hexamine solution (4% hexamine, 2% NaOH in water) at 1 l/min.

Since the whole of the sample can be titrated, greater sensitivity can be obtained by sampling at 10 l/min. through a larger volume of absorbing solution, in either a bead or a dimple bubbler.

REAGENTS }
METHOD } See chloride by potentiometric titration.

SECRET

33. PHOSPHORUS SMOKE (P_2O_5) (1951)

USE

The white cloud produced by burning white phosphorus has been used as a comparatively innocuous tracer in many trials.

PRINCIPLE

The phosphorus is converted to ammonium phosphomolybdate, which is then reduced in the presence of acid to give a blue colour.

COLLECTION

Samples are taken in filters fitted with Whatman No.1 filter paper, aspirated at 10 or 15 l/m.

REAGENTS

- (i) 1.25 N sulphuric acid
- (ii) 9.5% ammonium molybdate
- (iii) 40% stannous chloride. 40 g $SnCl_2$ dissolved in 86 ml conc. HCl and made up to 100 ml with more conc. HCl. This solution should be kept in the dark and should not be stored for more than 1 month.
- (iv) 2% stannous chloride. 1 ml of the 40% solution diluted to 200 ml with water. This solution should be freshly made as required and should not be stored for more than an hour or two.

METHOD

The filter paper is placed in a boiling tube, 10 ml 1.25 N H_2SO_4 added and shaken, and the tube placed in a boiling water bath for 4 mins. The contents are then filtered into a tube graduated at 8 ml until the volume of the cool filtrate is 8 ml. (i.e. a $4/5$ aliquot of the whole). The whole 8 ml is used, or a suitable smaller aliquot made up to 8 ml with more 1.25 N H_2SO_4 . 1 ml of ammonium molybdate solution and 1 ml dilute stannous chloride solution are added and the mixture shaken (Note: the temperature should not be below $15^{\circ}C$ and the molybdate and stannous chloride solutions should be blown from the pipettes into the main solution to give good and rapid mixing.) After standing for 5 minutes, the colour produced is measured on the Spekker using the No.1 red screens.

Blanks should be done on uncontaminated filter paper.

CALIBRATION CURVE

See G agents by phosphate.

SECRET

34. SALICYLALDAZINE (1953)

USE

Salicylaldazine is used as an innocuous tracer, particularly in built-up areas.

The main method of analysis is a physical one, depending on the fluorescence of the solid compound. Chemical analysis is required for any samples which are too heavy to be estimated physically, and also to confirm the strength of the samples used for the physical calibration curve.

PRINCIPLE

Salicylaldazine gives a yellow colour in sodium hydroxide solution, with which the other products of the smoke generator do not interfere.

Note The method using phospho-tungsto-molybdic reagent, similar to that used for methyl salicylate, was found to give erroneous results when the salicylaldazine was put up by a smoke generator.

COLLECTION OF THE SAMPLE

Samples are taken at 10 or 15 litres per min. in double cone filters using blue-asbestos filter papers.

REAGENT

0.1 N sodium hydroxide solution.

ANALYTICAL METHOD

The paper is placed in a flat bottomed dish 2½" or 3" in diameter, covered with 15 ml 0.1 N NaOH and rotated gently at intervals for 10 minutes. The solution is filtered and the colour measured in the Spekker using the 1 cm cells, and the No. 7 dark blue or the Spectrum violet 601 filters.

Blanks should be determined on similar blue asbestos paper.

Calibration curve

The calibration curve is prepared from a solution of salicylaldazine in 0.1 N NaOH.

SECRET

35. SULPHUR DIOXIDE (1953)

USE

Sulphur dioxide has been used as a readily available tracer gas.

PRINCIPLE OF THE METHOD

The colour produced with basic fuchsin and formalin is measured.

COLLECTION OF THE SAMPLE

Miniature bubblers charged with 5 ml water and operated at 1 litre/min. are satisfactory for sampling times up to 10 minutes, the slip being negligible. The solutions are stable for at least 3 days. (For longer period samples, or if it is desired to store the samples for longer than 3 days before analysis, it might be advisable to add a little pure glycerine to the water to retard oxidation of the sulphur dioxide, but this has not been tested.)

REAGENT

6 ml conc. sulphuric acid (S.g. 1.84) and 2 ml of an alcoholic solution of basic fuchsin (2%) are added to 115 ml water; After 5 minutes 0.2 ml 40% formalin solution is added.

ANALYTICAL METHOD

3 ml of water are added to the sample, followed by 1 ml of reagent, the mixture is stirred and allowed to stand for 20 minutes. The colour is then read on the Spekker using the 1 cm or the 0.25 cm cells and the No.5 green screens.

CALIBRATION

Typical results:

$\mu\text{g SO}_2$		8	16	24	40	48	80	120	200
Spekker	1 cm cell	0.34	0.56	0.74		1.11			
Reading	0.25 cm cell				0.31		0.50	0.64	0.78

SECRET

36. ZINC (1954)

USE

Zinc cadmium sulphide is used as an innocuous smoke to investigate the long distance travel of particulates. Traces of material found at these distances are estimated by solid fluorescence measurement, but for an estimation of the "fall-out" near the source the quantities are too great to be measured by this means and a chemical method is used.

PRINCIPLE OF THE METHOD

When excess quinaldinic acid is added to a zinc solution in an acetate buffer, zinc quinaldinate is precipitated. The excess of quinaldinic acid can then be titrated with a standard zinc solution and the end point determined by measuring the change in the diffusion current using a dropping mercury electrode. Cadmium does not interfere as cadmium quinaldinate is not precipitated at the pH of the buffer used.

It is not convenient to titrate zinc directly with quinaldinic acid, since in the presence of an excess of zinc the precipitation is very slow and the diffusion current takes a long time to stabilise after each addition of titrant.

COLLECTION OF THE SAMPLE

The samples are collected in petri-dishes, which are covered before transportation to the laboratory.

APPARATUS

See figure 27

For details see P.T.P. 342.

REAGENTS

- (i) Acetate buffer pH 5.2 50 ml N sodium acetate and 10 ml N HCl made up to 250 ml.
- (ii) 0.1 M ZnSO_4 for 300 μg to 3,200 μg Zn
- (iii) 0.01 M ZnSO_4 for 30 μg to 320 μg Zn
- (iv) 0.0025 M ZnSO_4 for 8 μg to 80 μg Zn
- (v) 0.05 M Quinaldinic acid for 300 to 3,200 μg Zn
- (vi) 0.0025 M Quinaldinic acid for 8 to 320 μg Zn

METHOD

The zinc cadmium sulphide is dissolved by heating with a little concentrated hydrochloric acid and if necessary a few drops of nitric acid. It is then washed from the petri-dish into a small conical flask and evaporated just to dryness on a hot-plate, redissolved in distilled water and evaporated again to remove any traces of acid. It is then dissolved in the acetate buffer and washed into the titration cell with more buffer, keeping the volume as low as possible.

SECRET

An estimate of the amount of zinc likely to be present is made and the appropriate amount of quinaldinic acid is added,

2 ml 0.05 M for 300 μ g to 3,200 μ g Zn

4 ml 0.0025 M for 30 μ g to 320 μ g Zn

1 ml 0.0025 M for 8 μ g to 80 μ g Zn

The cell is then placed in the burette stand, clean mercury added to form a pool about $\frac{1}{4}$ " deep, the contact wire to this pool, the dropping mercury electrode, the air stirrer tube and the burette placed in position. The battery, previously calibrated against the Weston Cell, is set to apply 1.50 volts across the titration cell. The backing out resistance is adjusted and the sensitivity control set at 3 for the high range, 12 for the medium range and 20 for the low range.

Additions of 0.05 ml of standard zinc solution (either 0.1 M, 0.01 M, or 0.0025 M, as appropriate) are made, the solution stirred after each addition by blowing a little air through the stirrer tube from a blow bulb, and the galvanometer reading noted as soon as it has become steady (this will take about 1 minute for the high or medium range and about 2 minutes for the low range). If the diffusion current is found to increase when the first addition of the standard zinc solution is made, insufficient quinaldinic acid has been added, and more of this reagent should be added before continuing the titration.

The galvanometer readings are plotted against the volume of titrant added and the intersection of the two straight lines is taken as the end point.

The amount of zinc is then found by calculation, e.g. for the high range:

If T_H is the volume of 0.1 M Zinc used in the back titration

$$\begin{aligned} 2 \text{ ml } 0.05 \text{ M quinaldinic acid} &= 2 \times 0.025 \text{ ml M zinc} \\ &= 0.5 \text{ ml } 0.1 \text{ M zinc} \end{aligned}$$

$$\text{Hence: } \mu\text{g Zn in sample} = (0.5 - T_H) \times \frac{0.1 \times 65.4}{1,000} \times 1,000,000$$

$$= 6540 (0.5 - T_H)$$

For the medium range: T_M .. volume of 0.01 M Zn

$$\mu\text{g Zn in sample} = 654 (0.5 - T_M)$$

For the low range: T_L .. volume of 0.0025 M Zn

In this range there is a blank reading of 0.05 ml 0.0025 M Zn, for which a correction must be made

$$\mu\text{g Zn in sample} = \frac{654}{4} (0.5 - B1 - T_L)$$

$$= 163.5 (0.45 - T_L)$$

SECRET

SECTION IV

MECHANICAL AIDS IN LARGE SCALE SAMPLING

1. The Bubbler Charging Machine (Fig.29)

Two hypodermic syringes are connected by means of a four-way tap to a reservoir of solvent and to an outlet, the tap being so arranged that when one syringe fills, the other empties. A fixed stop with a fine screw adjustment is provided above each syringe so that the plunger is stopped when the syringe has filled to the correct graduation mark. A considerable head is required in order to fill the syringes rapidly and it has been found advantageous to fix a weight to the top of the plunger to hasten the emptying.

After the air bubbles have been removed from the system, the volume of solvent delivered is very accurate, and it has been found that not only is the bubbler charging carried out more expeditiously, but it is also more accurate than when either burettes or pipettes are used, even with less skilled personnel operating the machine.

Duplicate machines have been constructed with 2 ml syringes and with 5 ml syringes - the two volumes of solvent most commonly used in bubblers.

2. Bubbler Airlers (Decontamination Racks) (Fig.30)

These airlers are built on the clothes horse principle, but with rows of hooks along each side of each horizontal bar. One rack with 5 rows of 10 hooks on each side will hold 100 bubbler frames, i.e. 300 bubblers when using triple frames. When using single frames, more than one bubbler is hung on the same hook.

After sampling, the contaminated bubblers are removed from the slotted boxes and hung on these racks, in the open air. The racks are then carried into a warm ventilated chamber, left overnight and taken to the analytical laboratory next morning.

Since using this decontamination system, the analytical teams have not shown any symptoms of G agent poisoning, but overnight airing has not always been sufficient for bubblers which were heavily contaminated with mustard gas.

3. Bubbler Washing Machine (Fig.31)

A water pump is used to force distilled water from a reservoir through a manifold into jets. These jets are connected to the manifold by rubber bungs in which drainage slots have been cut, thus giving a flexible connection and permitting rapid handling without casualties. The water overflow is collected in a trough.

The bubblers are rinsed in tap water and then placed over the jets which direct the water to the end of the bubbler. 10 bubblers are accommodated at once.

1111

SECRET

4. The Stem Washing Machine (Fig. 32)

The capillary inlet tubes (or stems) of the bubblers are washed in a machine which employs the cascade counter current principle. The stems are placed in an expanded aluminium basket which is then placed in a container in the cascade stand. Hot water flows into the bottom of the first container, out at the top and into the bottom of the second and so on. The bubbler solvent - cyclohexanol - is lighter than water and is thus removed from the capillaries by floatation as well as by the solvent action of the water.

The basket of stems is placed in the lowest (4th) container first, then when another basket of stems is ready the first basket is moved up to the third container and the second basket placed in the lowest container, etc. After a few minutes in the top container the basket of stems is allowed to drain, given a thorough rinsing in distilled water and the stems are then ready to dry.

5. Bubbler and Stem Dryer (Fig. 33)

An air blower is used to blow air over a heater and then into a manifold where it is distributed into 50 tubes. These aluminium tubes are of such a size ($11/32$ inch outer diam. and $9/32$ inch inner diam.) that either bubblers can be placed over them or the capillary tubes of the stems can be placed inside, so that the same machine can be used to dry either bubblers or stems or a mixture of the two. The bubblers rest on rubber tubing which connects the tubes to the manifold and the capillary tubes are prevented from seating on the top of the aluminium tubes by a dimple near the bottom of this tube arranged to allow some of the hot air to pass outside the capillary as well as to go through.

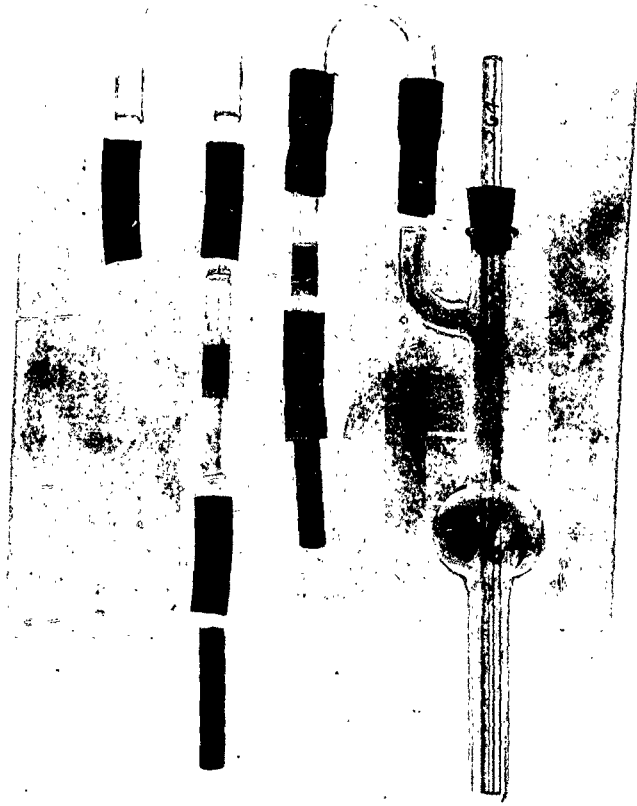


FIG.1.

MINIATURE BUBBLER.

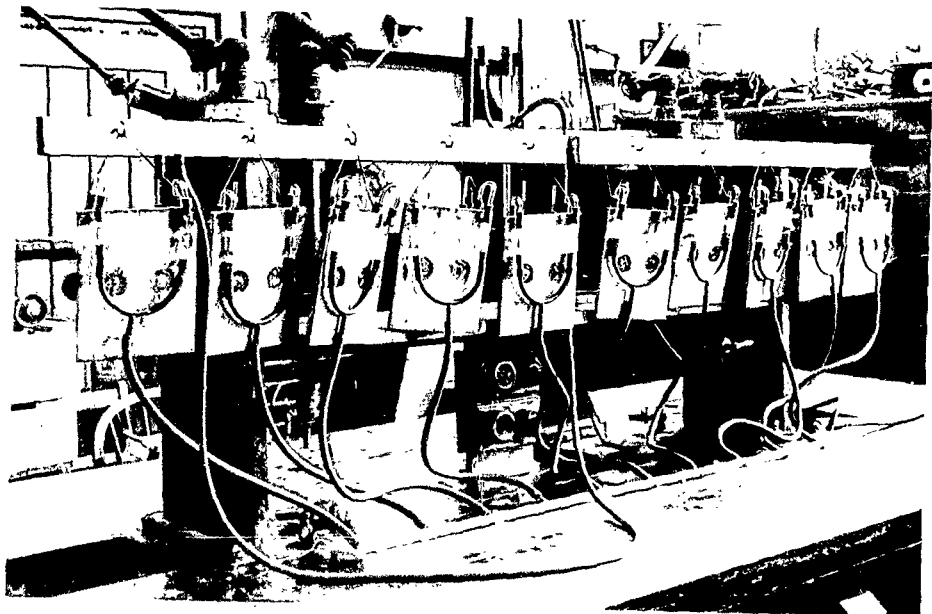


FIG.2.

MINIATURE BUBBLER - CHECKING FOR FLOUR RATE.

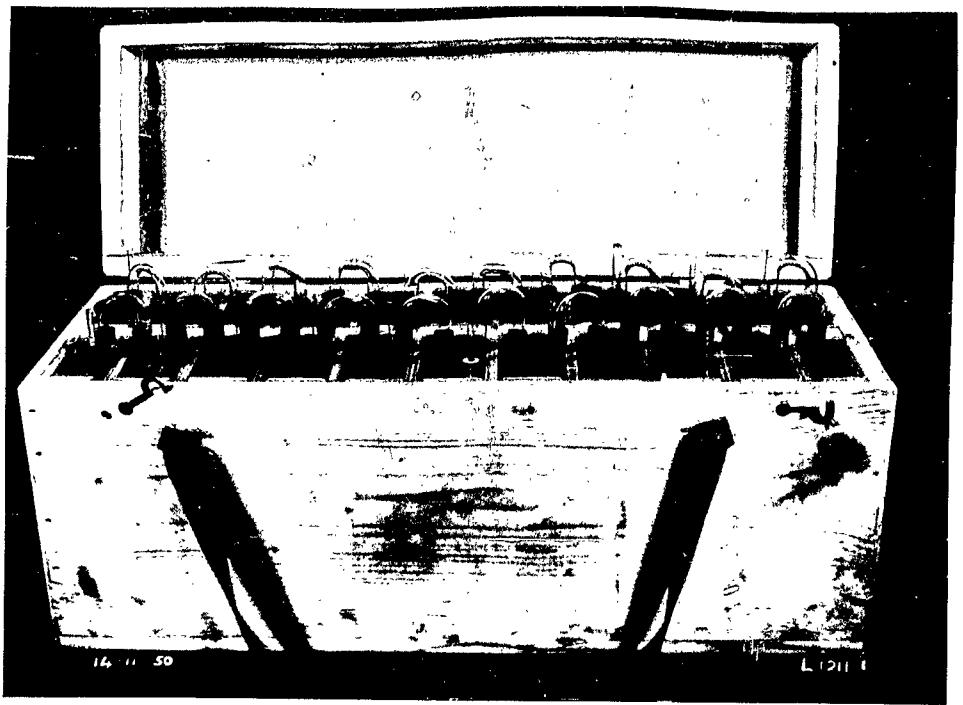


FIG. 3. MINIATURE BUBBLER
 METHOD OF CARRIAGE.

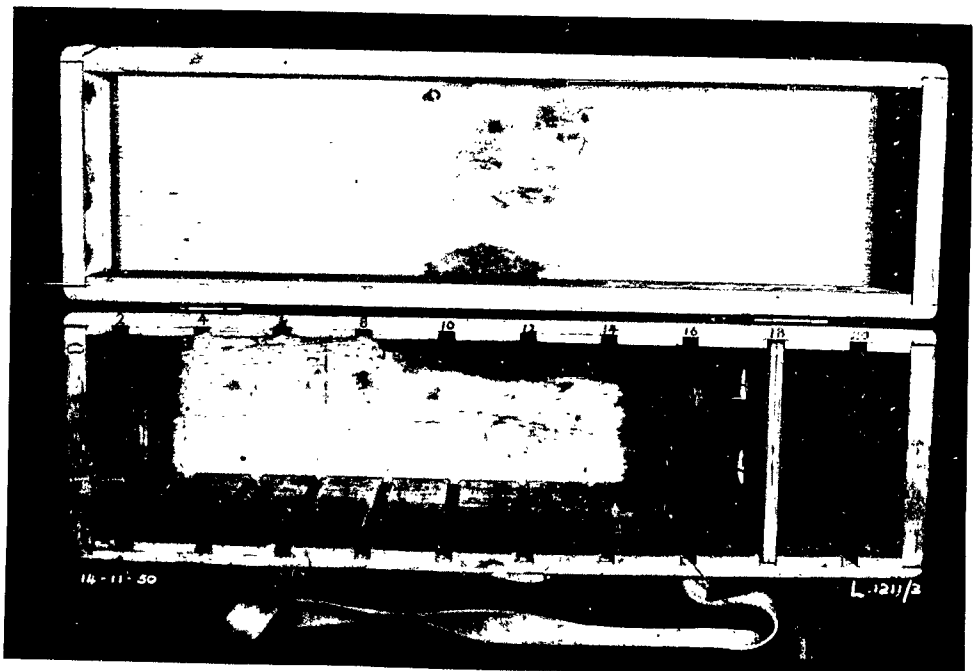


FIG. 4.

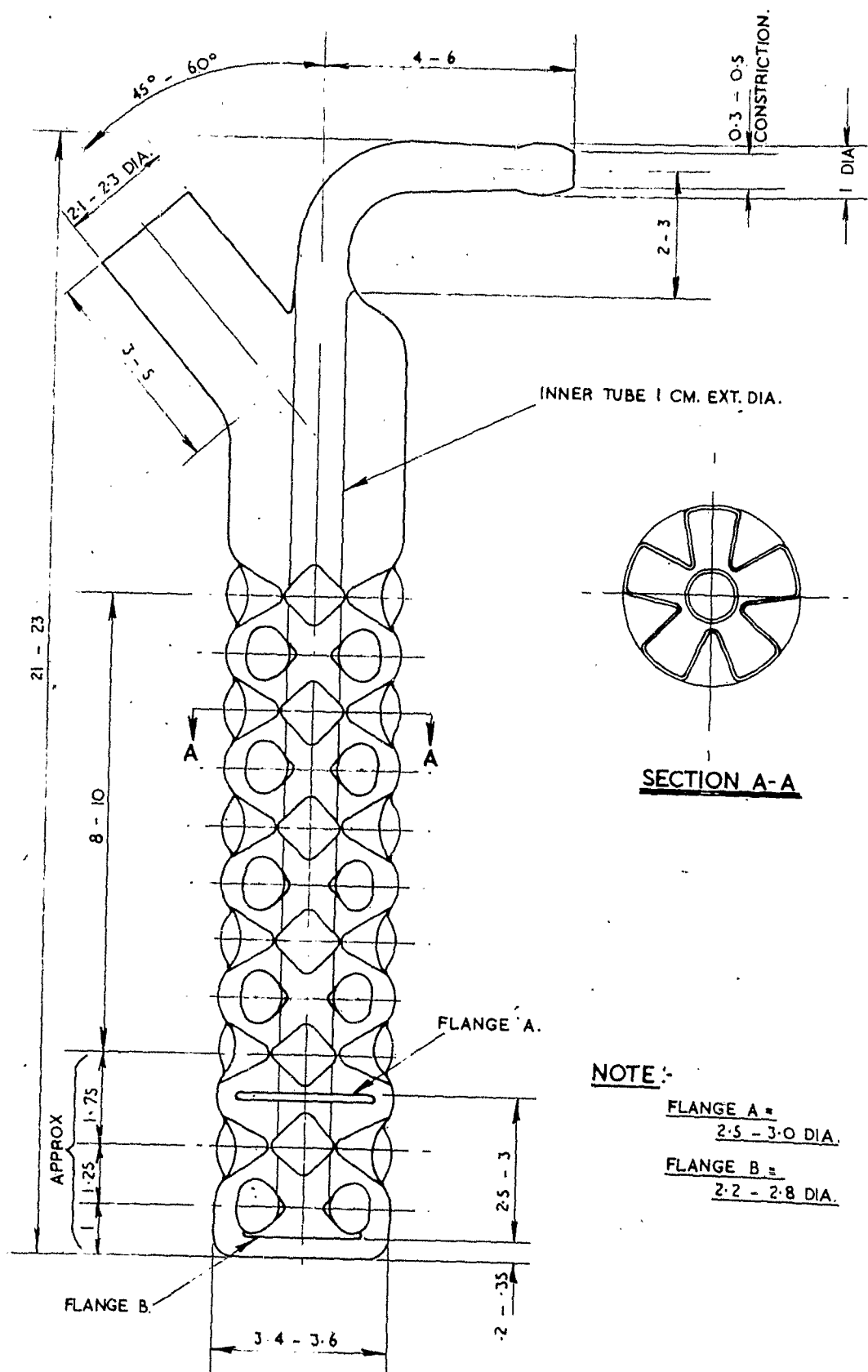
FIG. 5



MINIATURE BUBBLER
FIELD INSTALLATION

FIG. 6.





NOTE:-

FLANGE A =
2.5 - 3.0 DIA.

FLANGE B =
2.2 - 2.8 DIA.

DIMPLE DISC BUBBLER

MATERIAL: PYREX GLASS.

FIG. 7.

DIMENSIONS ARE IN INCHES

C.P.B. J. A. R. M.E.S.
C.D.E.E. PORTON.

SCALE: 1/2
P 1713
DATE 2.3.55

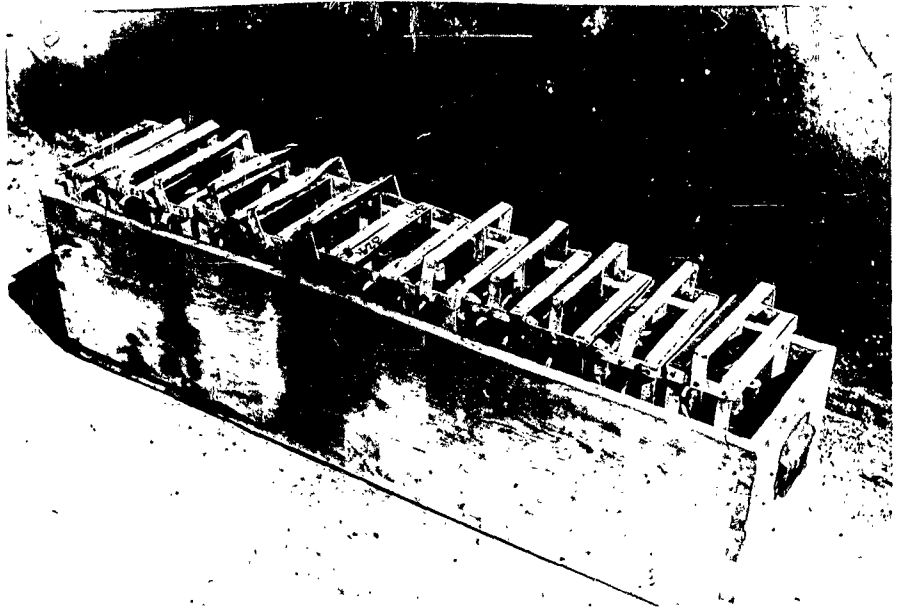


FIG. 8

DIMPLE DISC BUBBLER - METHOD OF CARRIAGE

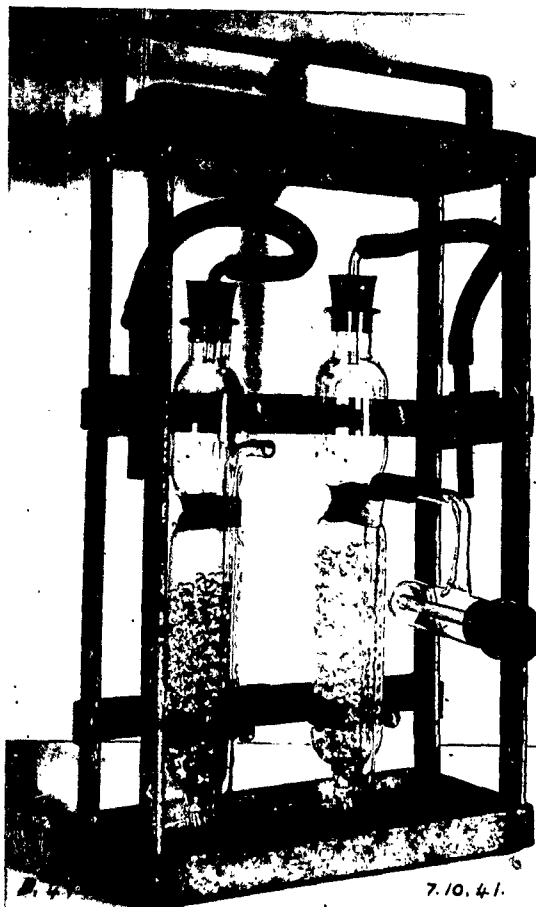


FIG.9.

BEAD BUBBLER

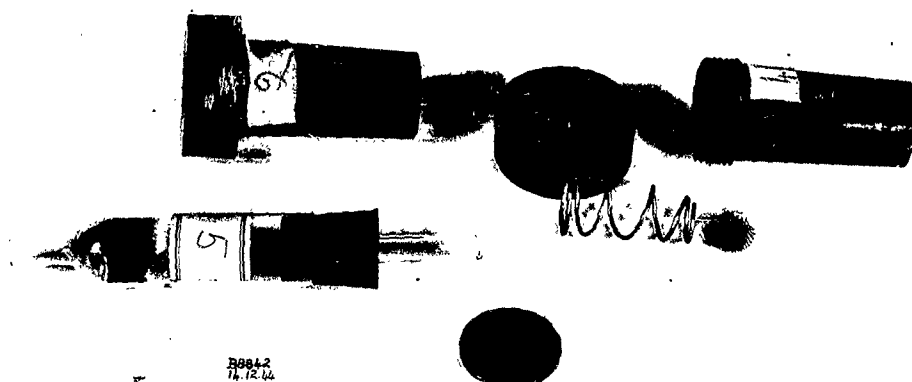


FIG.10. TUBE FOR SOLID ABSORBENTS

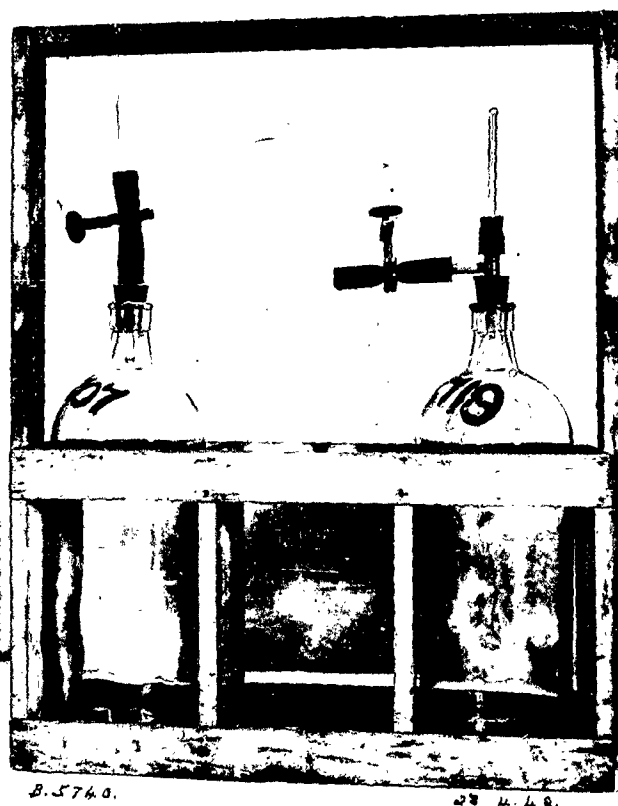
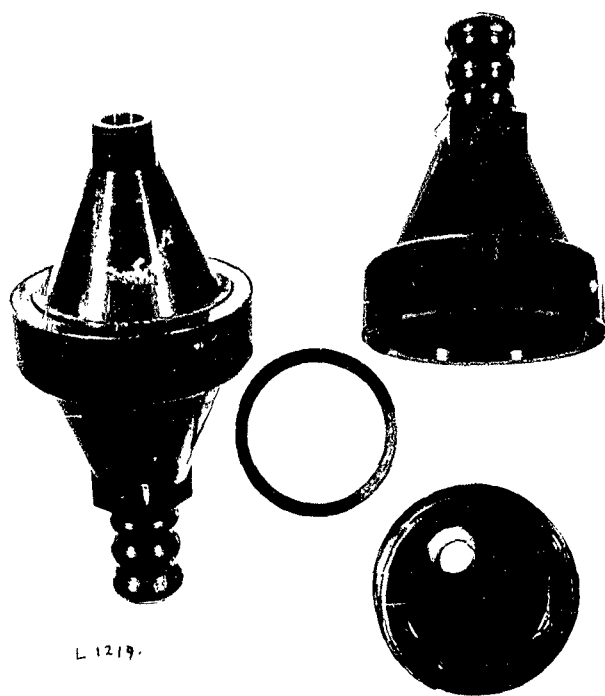
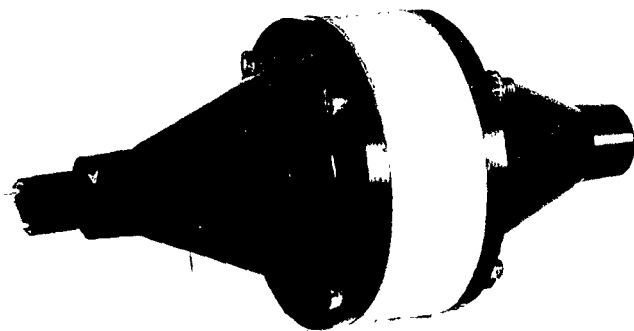


FIG.11. THE EVACUATED BOTTLE.



L 1219.

FIG.12. THE DOUBLE CONE FILTER.



B. 5470.

20.3.42.

FIG.13. DOUBLE CONE FILTER WITH GLASS TUBE FOR ISOKINETIC SAMPLING.

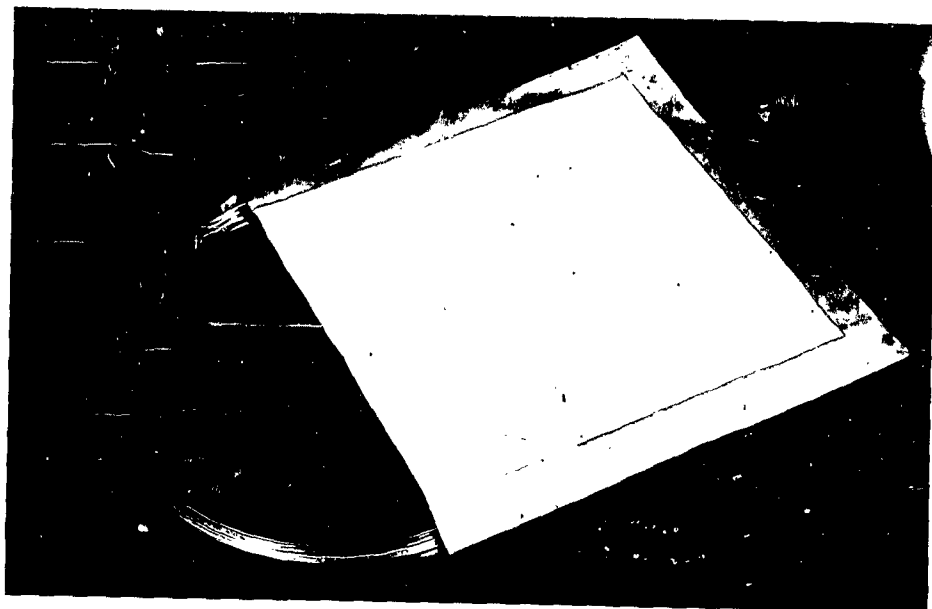


FIG.14.

SAMPLING ENVELOPE

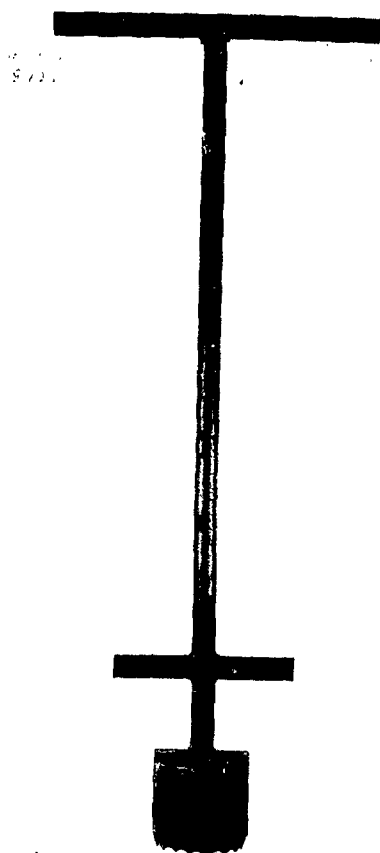


FIG.15 TURF CUTTER



- ALUMINIUM TUBING. 2" LONG 8 mm EXTERNAL DIAMETER.
- /// RUBBER TUBING 3" LONG 6 mm INTERNAL DIAMETER.
- == P. V. C. TUBING. 1/2" LONG 6 mm EXTERNAL DIAMETER.
- | VERIDIA DISC. 1/4" LONG { 8 mm EXTERNAL DIAMETER.
0.35 mm INTERNAL DIAMETER.

FIG. 16. VERIDIA DISC CRITICAL ORIFICE
ASSEMBLY.

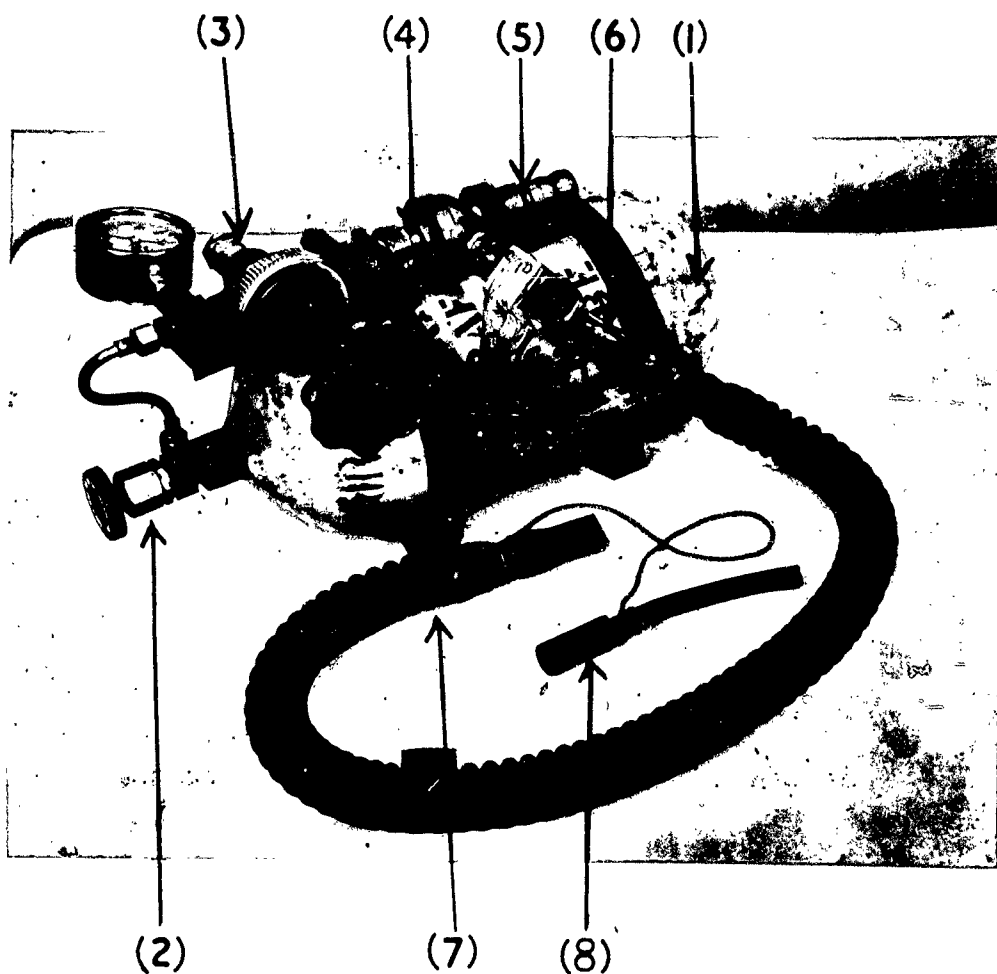
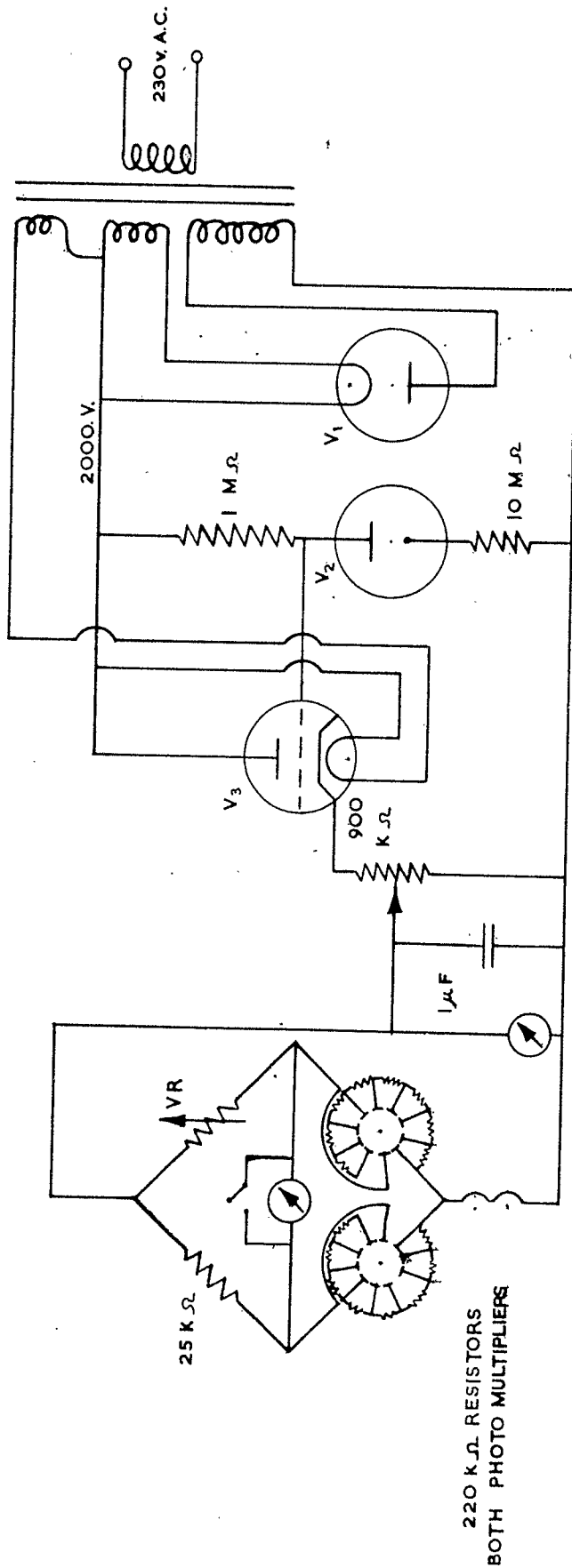


FIG. 17.
THE INJECTOR



V_1 = RECTIFYING VALVE V_3 = HALF OF 6SL7.
 V_2 = 900- μ A CORONA STABILISER. VR = 25-K Ω HELICAL POTENTIOMETER.

FIGURE 18. CIRCUIT DIAGRAM OF TWIN BEAM FLUORIMETER.

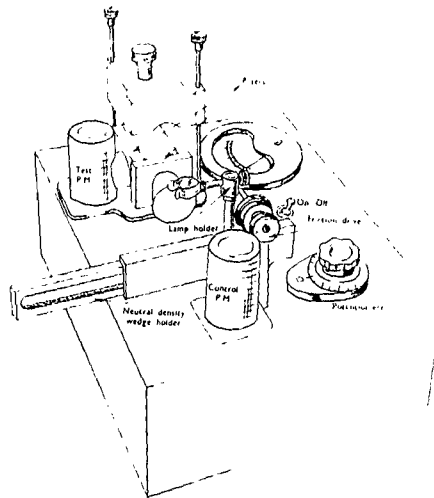


Fig.19 General view of apparatus

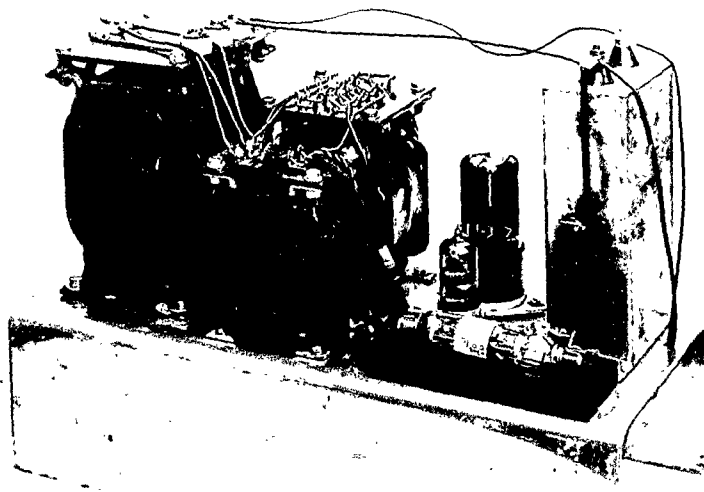


FIG.20. POWER PACK.

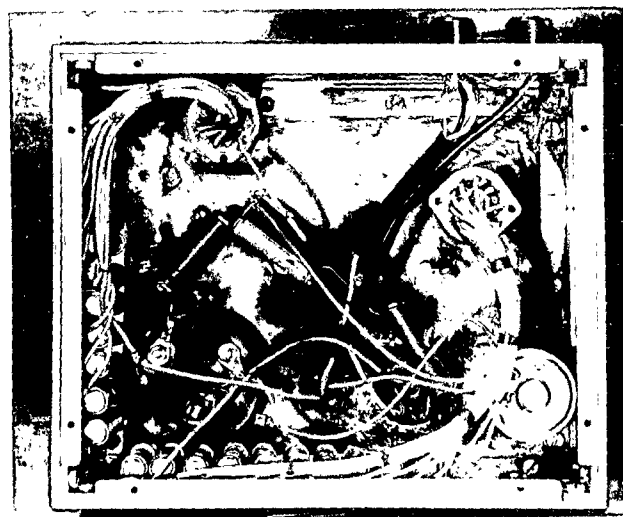


FIG.21. BOTTOM VIEW FLUORIMETER.

T. 1261/1.

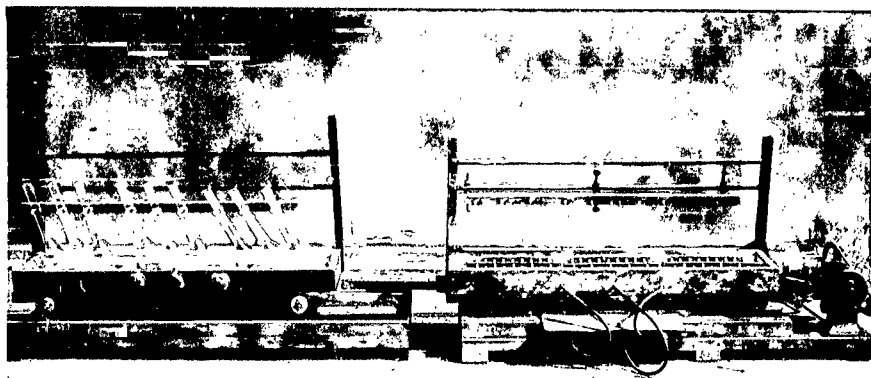


FIG.22 KJELDAHL FLASK SHAKER FOR USE IN
ARSENIC ANALYSIS.

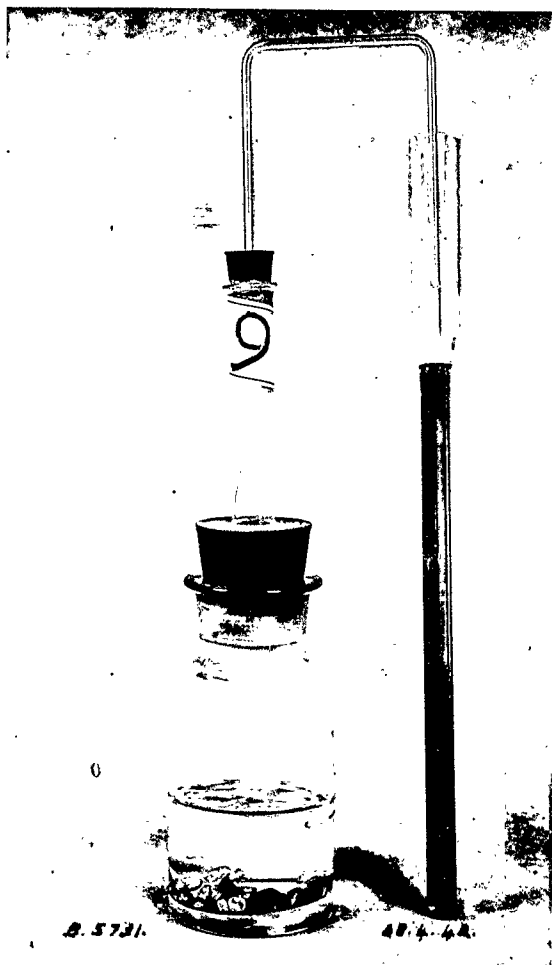


FIG.23. GUTZEIT POT FOR
ARSENIC ANALYSIS.

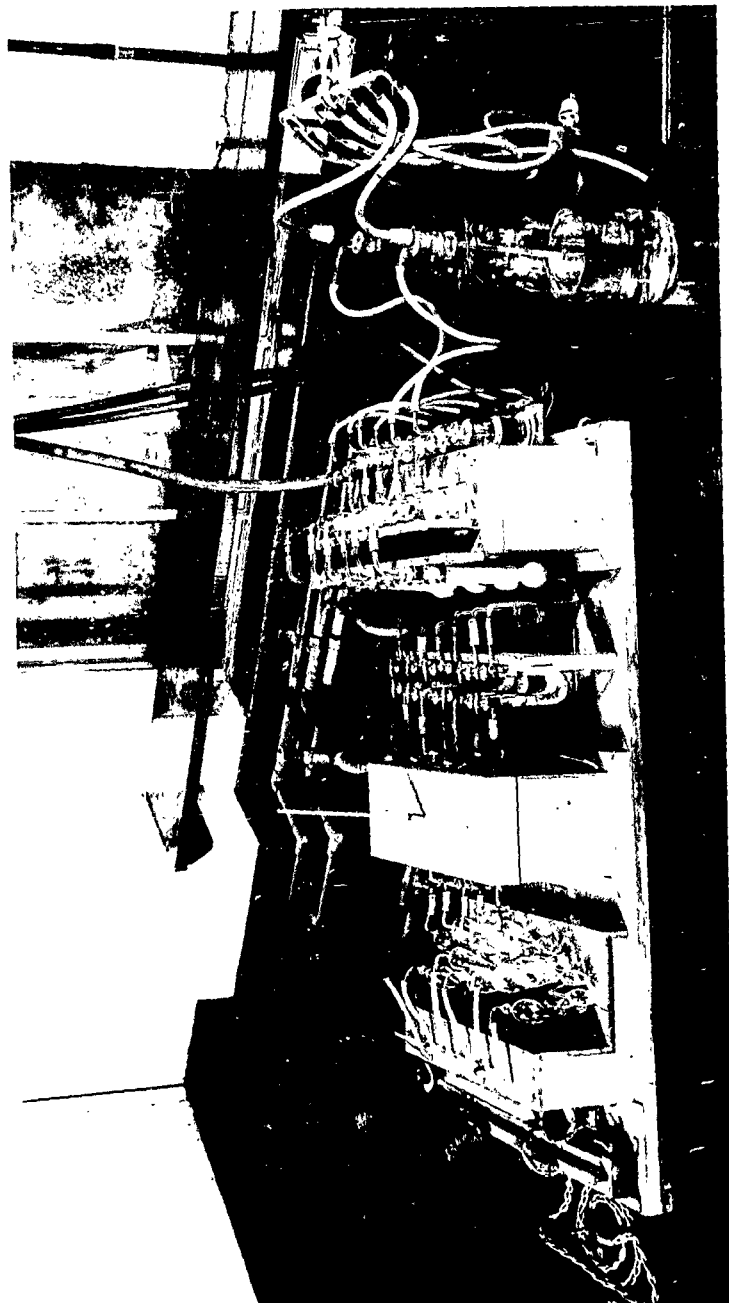


FIG. 24 IODINE PENTOXIDE TRAIN FOR CARBON MONOXIDE ESTIMATION

FIG. 24

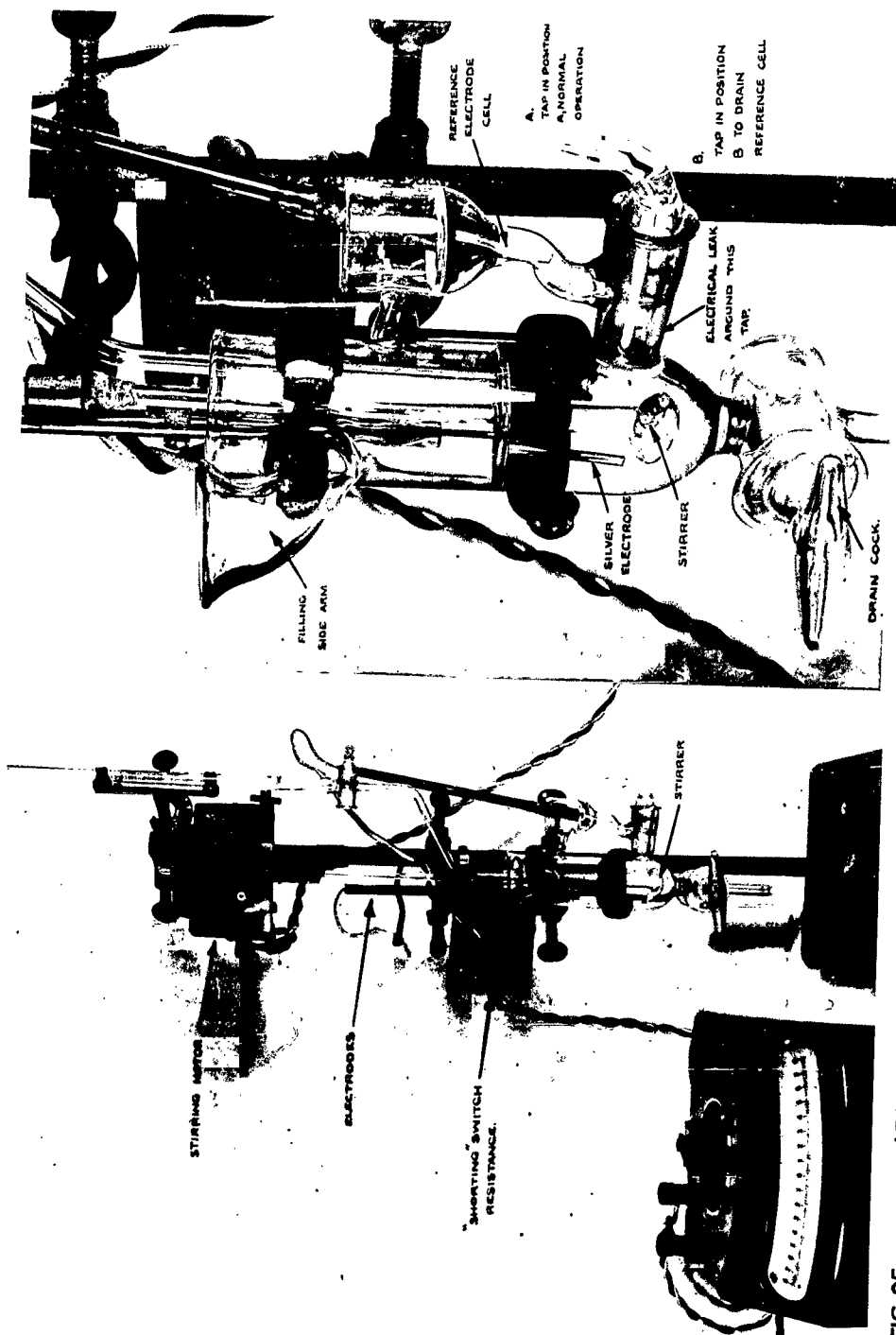


FIG. 25. APPARATUS FOR DETERMINATION OF CHLORIDE BY POTENTIOMETRIC TITRATION.

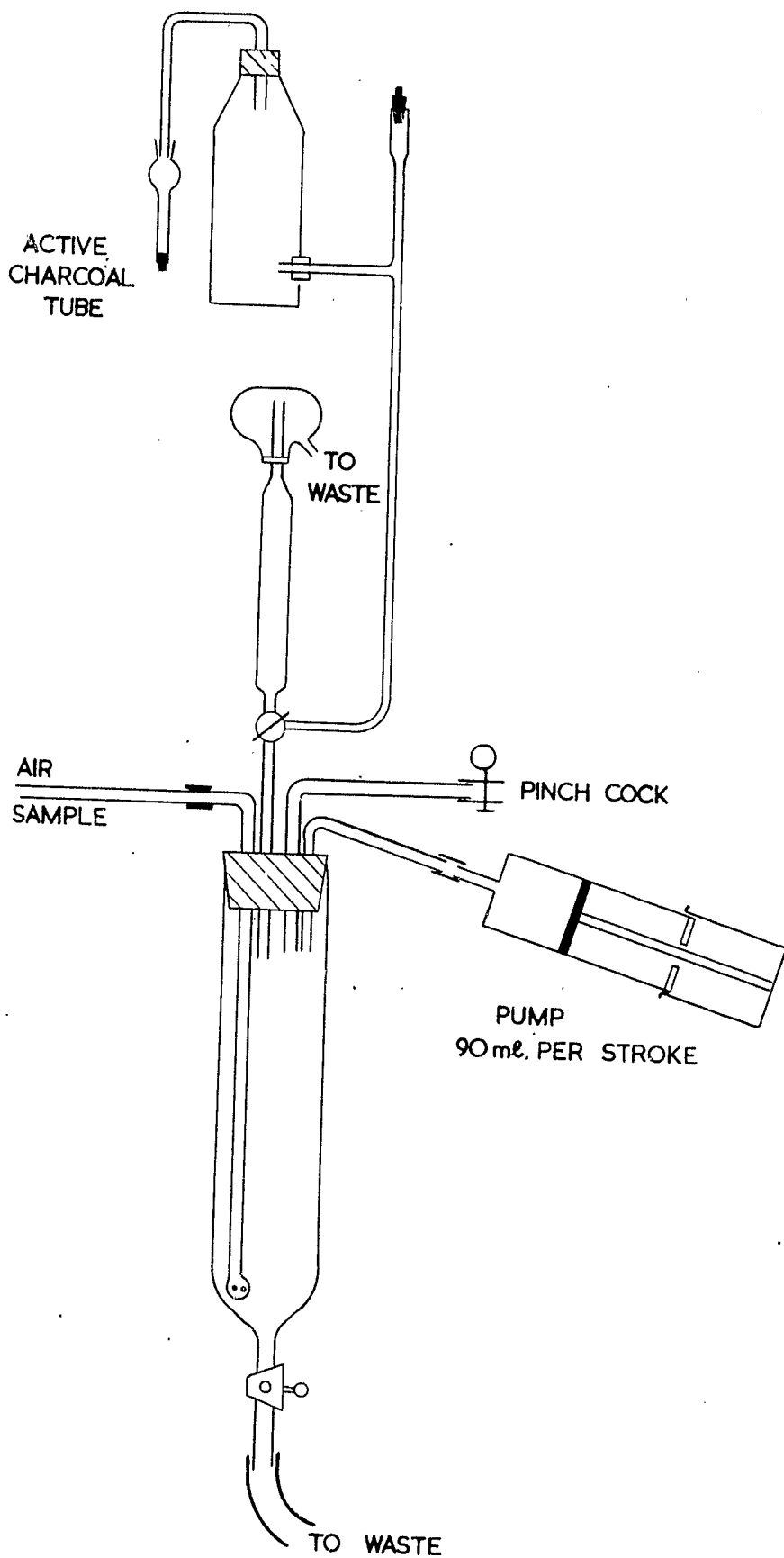


FIG. 26. THE CHLORIMETER

TC	<i>[Signature]</i>	M.E.S.
CK	<i>[Signature]</i>	C.D.E.E. PORTON.

PT 2607
DATE 6.3.56.

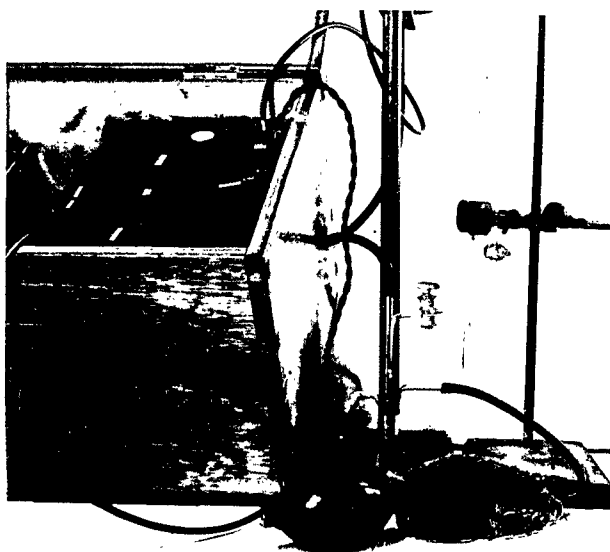
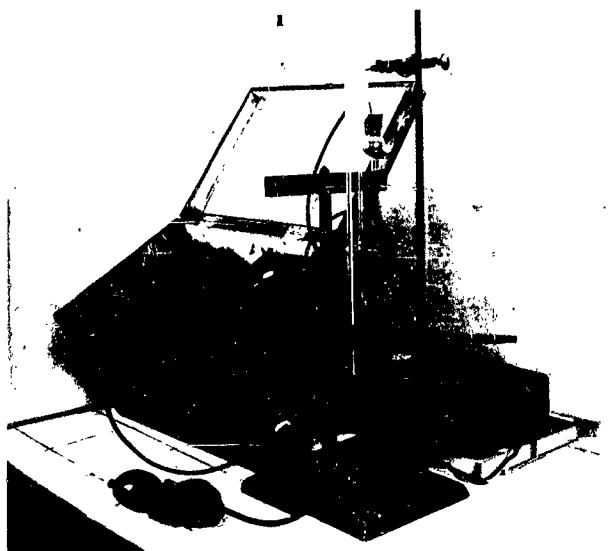
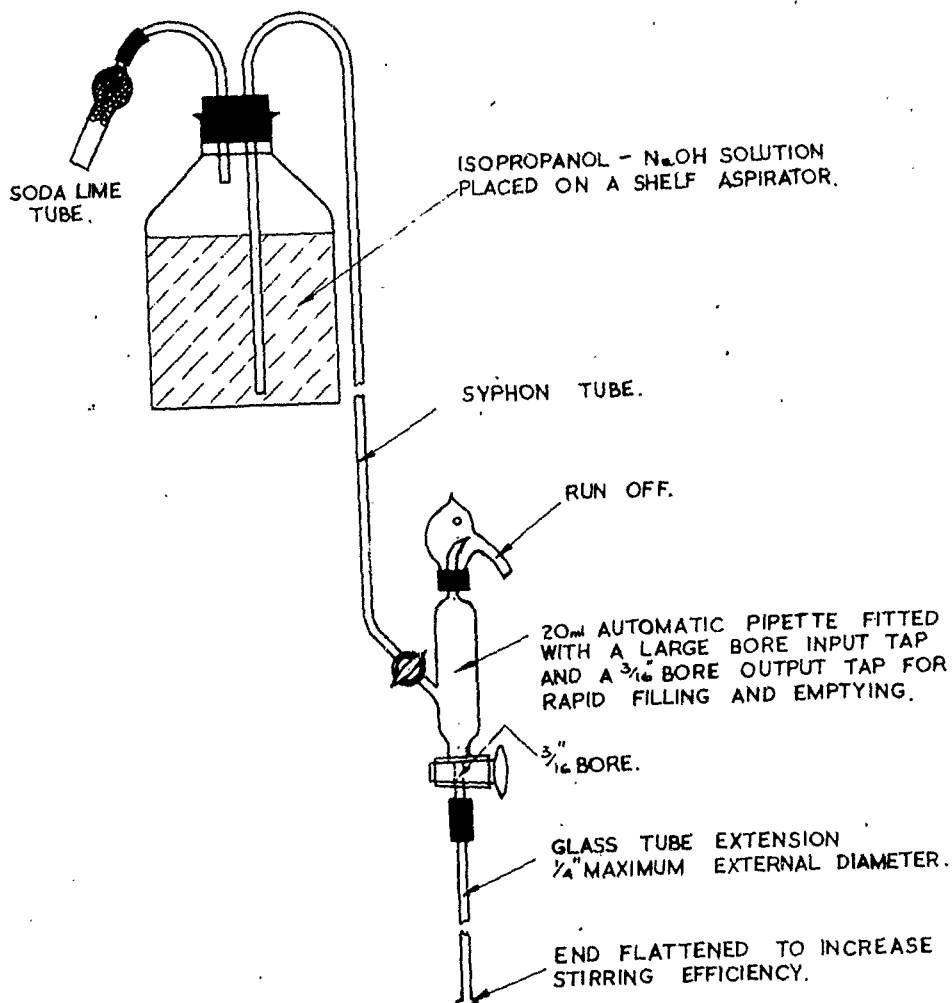


FIG. 27. APPARATUS FOR AMPEROMETRIC TITRATION OF FLUORIDE.



**FIG. 28. AUTOMATIC PIPETTE ASSEMBLY
FOR METHYL ACETOACETATE ANALYSIS.**

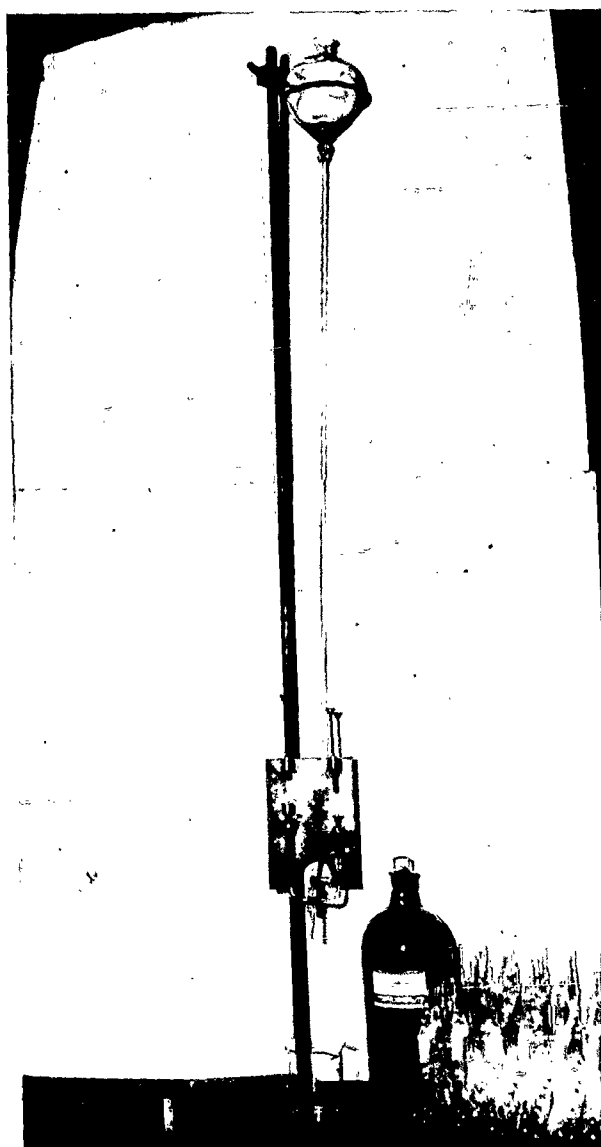


FIG. 29. BUBBLER CHARGING MACHINE.

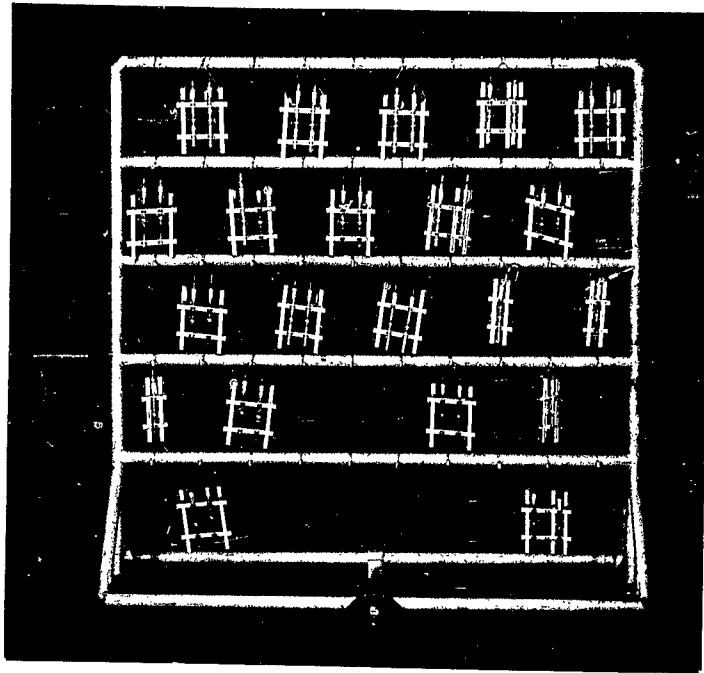


FIG. 30.

BUBBLER AIRER

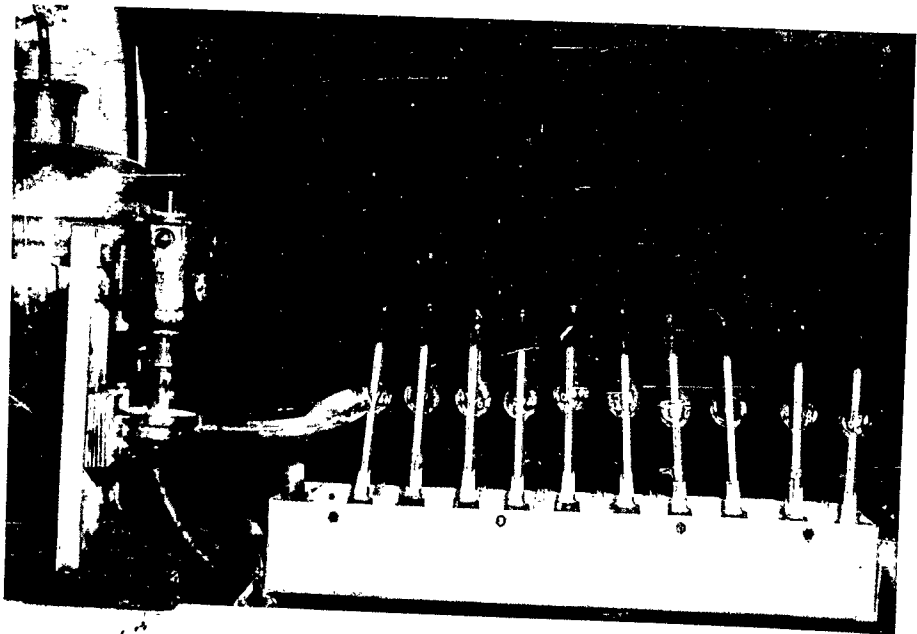


FIG. 31.

BUBBLER WASHING MACHINE.

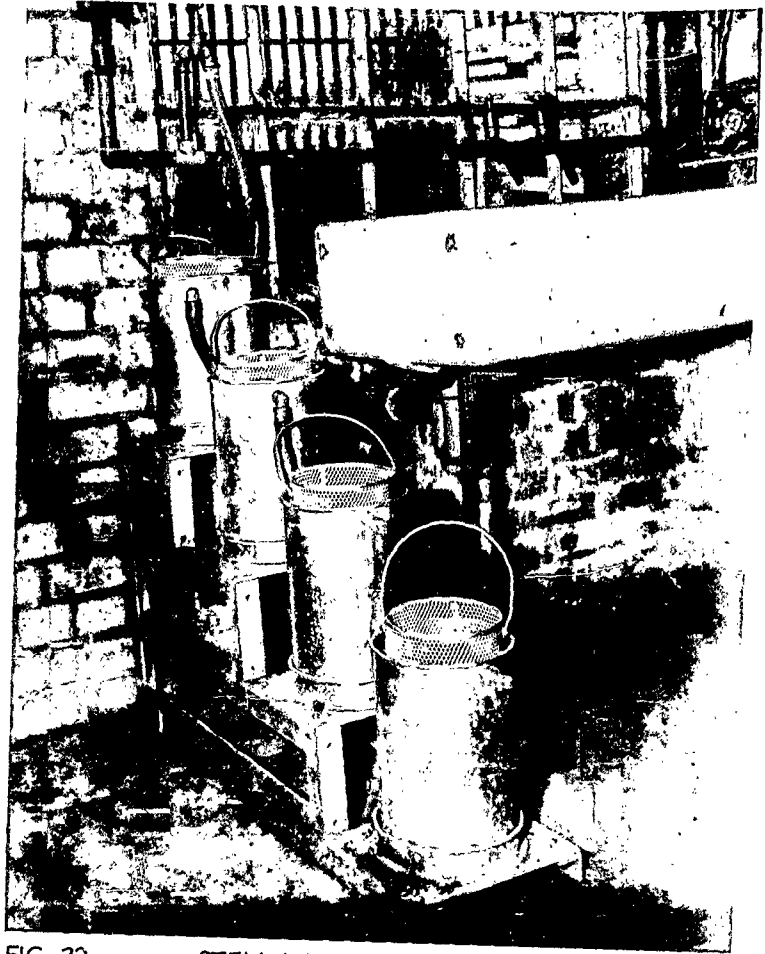


FIG. 32. STEM WASHING MACHINE

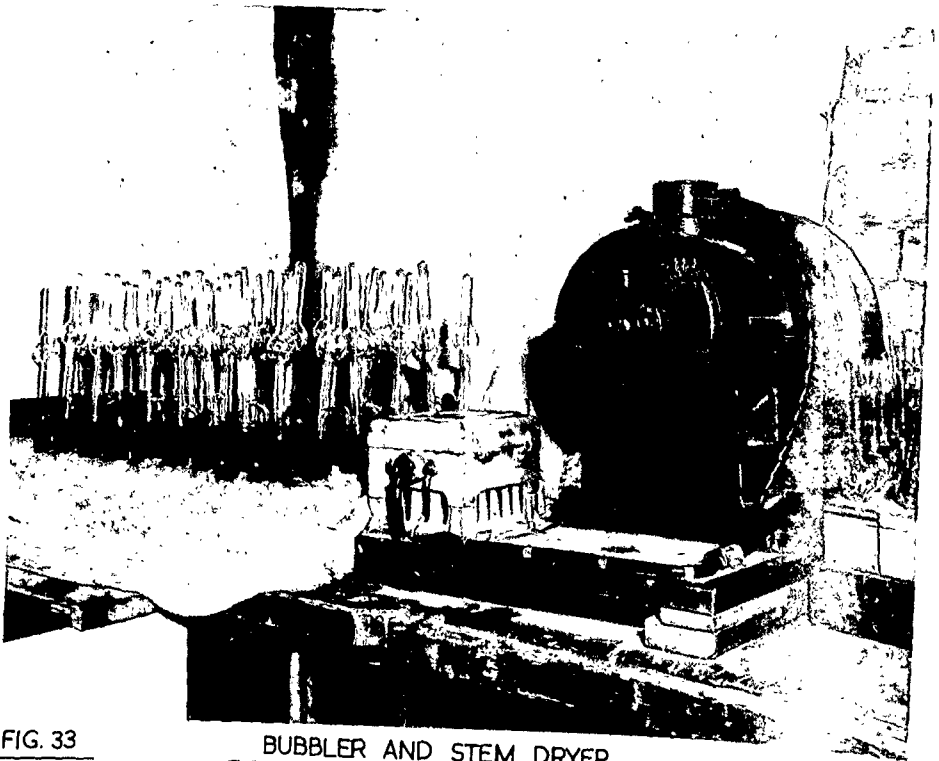


FIG. 33 BUBBLER AND STEM DRYER.

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